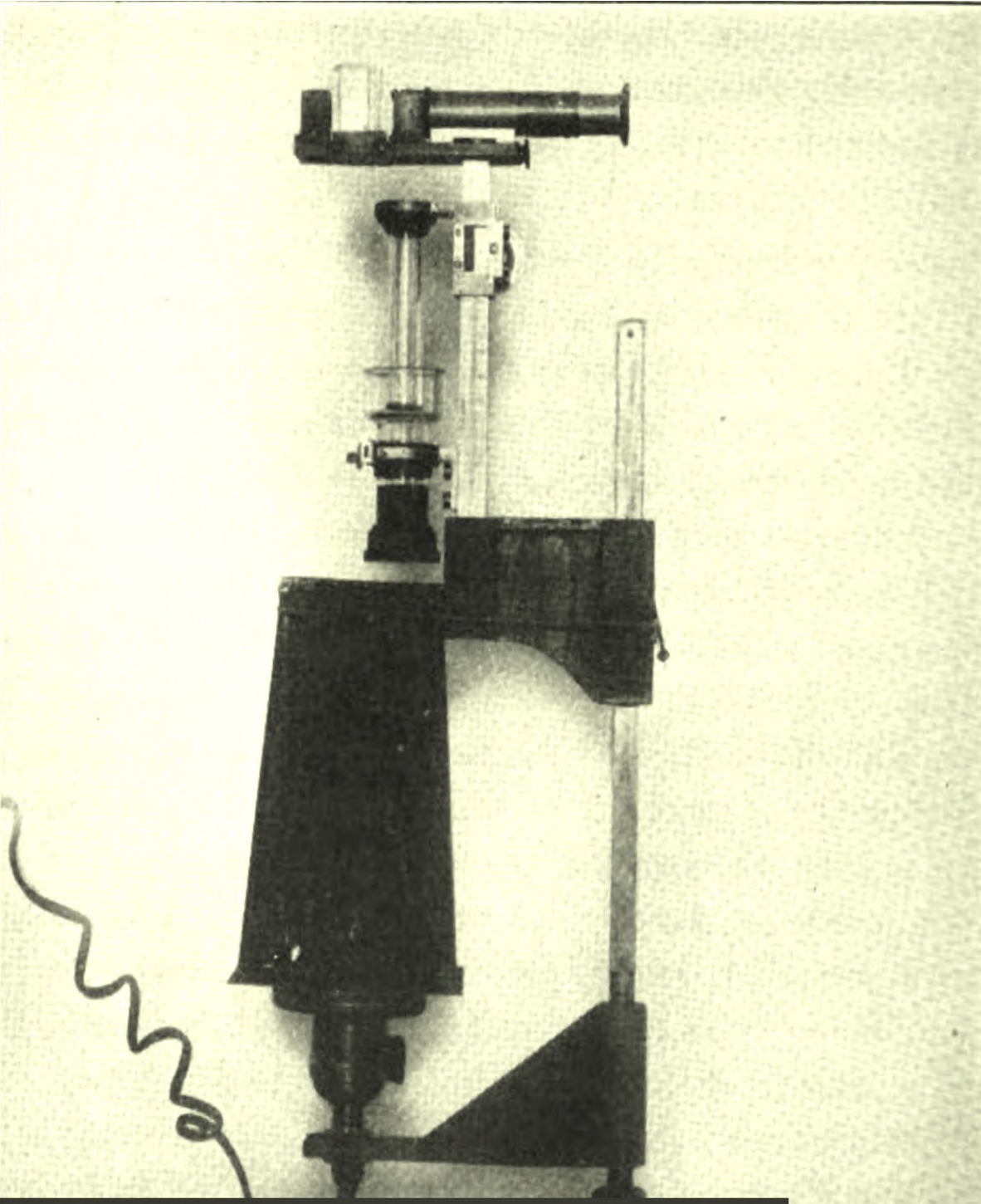
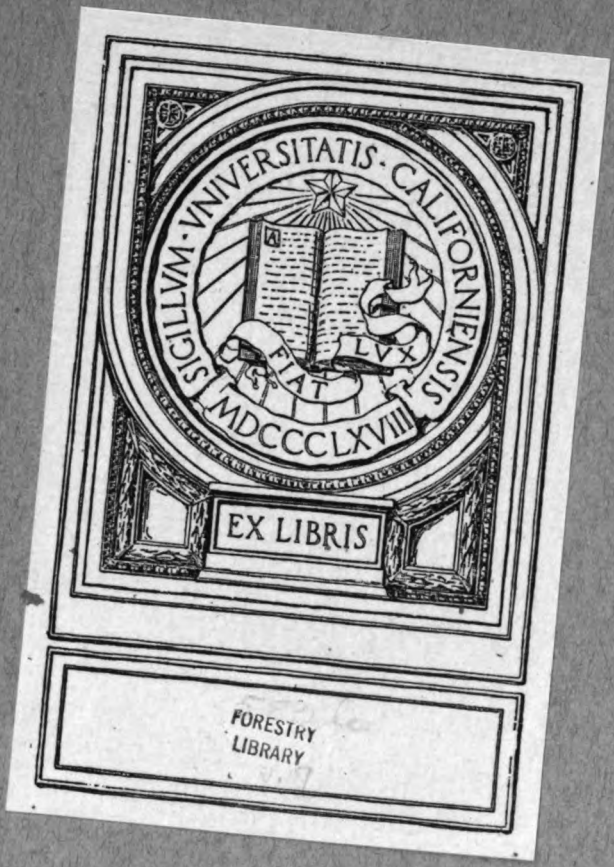


Journal

American Leather Chemists Association

Digitized by Google



Digitized by Google

Digitized by Google

Digitized by Google

The Journal of the

American Leather Chemists

Association

VOLUME IX, 1914

PUBLISHED MONTHLY BY
THE AMERICAN LEATHER CHEMISTS
ASSOCIATION

THE CHEMICAL PUBLISHING CO., PRINTERS
EASTON, PA.

Digitized by Google

TS947
A6
v.9
FORESTRY
LIBRARY

Digitized by Google

The Journal of the

American Leather Chemists Association

INDEX TO VOLUME IX, 1914

In this index (P) indicates a patent, and (A) an abstract.

INDEX OF AUTHORS' NAMES

ABT, GEORGES, Anthrax Disinfection, (A) 264
ABT, GEORGES, Salt Stains, (A) 272
ALLEN, W. H., Method of Storing Hides, (P) 382
ALSOP, W. K., President's Address 14, 500
ALSOP, W. K., Determination of Insolubles in the Analysis of Tanning Extracts 465
ALSOP, W. K., Standard Forms for Reporting Analyses 479
APPELIUS, W., AND R. SCHMIDT, Use of Cinchonine for the Detection of Sulphite-cellulose, (A) 566
ARDERN, E., AND W. T. LOCKETT, Oxidation of Sewage, (A) 331
ARMSTRONG, P. M. C., Melting Point of Stuffing Greases 326
ARMSTRONG, P. M. C., Recovery of Grease 327

BACHTENKIRCHER, H. E., Hydrated Lime, (A) 63
BAHLMANN, C., Determination of Hardness in Natural Waters, (A) .. 198
BALDERSTON L., Filter Method of Tannin Analysis 238
BALDERSTON, L., Methods of Chromium Determination 255
BALDERSTON, L., A New Form of Evaporator and Dryer 442
BALDERSTON, L., AND W. K. ALSOP, Laboratory Apparatus for Leaching Experiments 484
BALDRACCO, G., (see Romana, C.).
BALLIN, MAX, The Danish Leather Industry 408
BARTOW, E., AND C. SCHOLL, Lime for Water-Softening, (A) 198
BASCH, E. E., Feed-Water Purification and the Permutit Process (A) 158
BENNETT, H. G., A Compact Kjeldahl Apparatus 394
BENNETT, H. G., Further Progress in Tannin Analysis, (A) 243
BENNETT, H. G., Some New Tests for Tanning Materials 436
BEVE CUDWORTH, The Interrelation between the A. L. C. A. and The National Association of Tanners 97
BLOCKEY, J. R., The Practical Interpretation of Analytical Results 362
BLOCKEY, J. R., AND P. V. MEHD, Sulphides in Lime Liquors 176
BONE, WM. A., Surface Combustion, (A) 416
BYSTRON, J., Iron-tanned Leather, (P) 127

CARR, OMA, Contract Analyses 139
CORIN, M. F., Water and its Purification for Tanning Purposes 143
COX, W. R., What Can We Do to Promote a Better Understanding Between the Tannery Chemist and the Tannery Superintendent? 509
CUTLER, H. G., Tannin Bearers of South America, (A) 242

342616

Digitized by Google

DELANEY, C. R., Report of Committee on Comparative Analysis..... 70
DESMOND, J. J., Quality or Quantity?..... 34
DICKERSON, W. H., Sulphite-cellulose Blends..... 489

EACHUS, CHARLES, Cutch, (A)..... 117
EGLENE, LEON, New Method for the Rapid Determination of Tannin in Chestnut Extracts, (A)..... 240
EITNER, W., Leather from Artificial Hide, (A)..... 121
EITNER, W., Tender Grain and its Prevention, (A)..... 122
EITNER, W., Alcohol Tannage, (A)..... 201
EITNER, W., Guara, (A)..... 241
ELLIS, CARLETON, Analytical Constants of Hydrogenated Oils, (A)... 197

FAHRION, W., Chemistry and Analysis of Fats for the Year 1913, (A) 333
FAUST, T. A., Report of Committee on Moellon Analysis and on Hard Greases 548
FISCHER, EMIL, Synthesis of Depsides, Lichen-substances and Tannins 280
Abstract of the same..... 164
FRASER, S., The Ox-Warble Problem, (A)..... 446
FRONTANILLA, J., Cattle Industry in Paraguay, (A)..... 164
FRONTANILLA, J., Tanning Materials of Paraguay, (A)..... 277

GARCON, J., Tannery Effluents and Their Purification, (A)..... 191
GEAKE, A., AND M. NIERENSTEIN, The Constitution of Tannin, (A)..277, 445
GULDEN, PAUL, Sulphite-cellulose as Tanning Agent, (A)..... 336

HENDRICK, E., The Colloid's Lament..... 248
HIGGINS, C. A., Collodion in Leather-finishing, (A)..... 374
HILDT, W., Decolorizing Tanning Extracts, (P)..... 125
HÖNIG, MAX, Tanning Material, (P)..... 126
HUGONIN, G., Chrome Soap in Chrome Leathers, (A)..... 379

ILJIN, L. F., Composition of Tannin, (A)..... 276
INNES, R. F., Relation between the Feel of Leather and its Appearance under the Microscope, (A)..... 374
INNES, R. F., Lime-arsenic Paints, (A)..... 416

JALADE, M., Free Sulphuric Acid in Leather, (A)..... 162
JETTMAR, J., Modern Alum Tanning, (A)..... 275
JOHNSON, J. Y., Tanning Process, (P).....201, 447

KELLEY, W. J., The Rehbein Method of Determining Free Sulphuric Acid in Leather 340
KERR, G. A., Detection of Mangrove..... 25
KERR, G. A., Color Valuation of Tanning Materials..... 451
KOHL, F., Leather Dictionary, (book notice)..... 61
KOHN-ABREST, E., Applications of Active Aluminum, the "Alungallines" 260
KOHNSTEIN, B., Distinction between Bark Tans and Wood Tans, (A) 119
KRESS, OTTO, Free Sulphuric Acid in Leather..... 79

LAMB, M. C., Colloidal Tannins..... 359
LAMB, M. C., Economical Leather Manufacture, (A)..... 242
LAMB, M. C., Analysis of Matter Adhering to Goat-skins, (A)..... 373
LAMB, M. C., Analyses of East India Leather, (A)..... 375
LAUFMANN, R., Distinguishing and Testing Tanning Extracts, (A)... 245
LEVI, LOUIS, AND A. C. ORTHMANN, Chromium Determination in

Digitized by Google

Leather, ... 328
LEVINSTEIN, I., Sulphonated Fats, Waxes, etc., (P)..... 127
LOCKETT, W. T., (see Ardern, E.).
LOCKWOOD, A. H., Conservation of Hides, (A)..... 63
LOVELAND, F. A., The Relation Between the Green Salted Weight and the White Weight of Various Portions of the Hide 463
LÜDECKE, C., Carnauba Wax, (A)..... 124

MCCANDLISH, DOUGLAS, AND J. A. WILSON, Determination of Alkaline Sulphides 203
MCNEIL, C. A., A Study in Yellow, (A)..... 243
MADRU, R., (see Thuau, U. J.).
MARCUSSON, J., AND G. MEYERHEIM, Unsaponifiable in Natural and Hardened Fats, (A)..... 334
MEHD, P. V., (see Blockey, J. R.).
MEUNIER, L., AND A. SEYEWETZ, Comparative Tanning Properties of Different Quinones, (A)..... 379
MOELLER, W., Sulphuric Acid in Leather, (A)..... 122
MOELLER, W., Sulphite-cellulose and its Detection, (A)..... 246
MULLER-JACOBS, A., Contribution to the History of a New Industry.. 234
MUMFORD, H. W., Cattle in Argentina, (A)..... 192

NICOLARDOT, PAUL, Determination of the Acidity of Leather, (A).... 377
NIERENSTEIN, M., Some Recent Advances in the Chemistry of the Tannins 227
NIERENSTEIN, M., WITH A. GEAKE, Constitution of Tannin, (A)...277, 445

OBERFELL, C. R., Industrial Chemistry and the Leather Industry..... 55
OBERFELL, C. R., Report of Committee on Oils and Fats..... 545
OBERFELL, C. R., AND L. M. RICHESON, Extraction of Tanning Materials in Copper and Glass..... 28
ORTHMANN, A. C., (see Levi, L. E.).

PAESSLER, J., Estimation of Free Sulphuric Acid in Leather, (A) .87, 243, 336
PAESSLER, J., Asahan Gambier, (A)..... 168
PAESSLER, J., Investigation of Cellulose Extracts, (A)..... 566
PARKER, CHARLES E., Power from Spent Tan, (A)..... 376
POLLAK, L., Decolorizing Agent for Tanning Extracts, (A)..... 271
POLLAK, L., Compounds for Tanning Skins, (P)..... 448
POLLAK, L., Contribution to the Knowledge of Chestnut Extract, (A) 571
POWARNIN, G., Active Carbonyl and Tannage with Vegetable Substances, (A) 567
PROCTER, HENRY R., The Equilibrium of Dilute Hydrochloric Acid and Gelatin 207
PROCTER, HENRY R., Color Measurement of Extracts..... 225
PROCTER, HENRY R., Forty Years Ago..... 354
PROCTOR, C. M., Spruce Extract in Tanning, (A)..... 242

REED, H. C., Color Valuation of Tanning Materials..... 170
REED, H. C., AND A. SCHUBERT, Pentoses in Tanning Materials and the Detection of Mangrove..... 131
RICHESON, L. M., (see Oberfell, C. R.).
RITTER, J. G., Patent Leather, (A)..... 191
RITTER, J. G., Low Rendement and its Cause, (A)..... 199
ROGERS, ALLEN, Notes on Depilating..... 42
ROGERS, ALLEN, The Dyestuff Situation in America..... 538

Digitized by Google

ROGERS, J. S., The Detection of Oak in Tannin Extracts and Leathers 525
ROGERS, J. S., AND F. P. VEITCH, Clarification of Leather Extracts.... 421
RÖHM, OTTO, Process of Depilating Hides and Skins, (P)..... 126
ROLANTS, E., Purification of Tannery Effluents, (A)..... 195
ROMANA, C., AND G. BALDRACCO, The Salting of Hides, and Avoidance of So-called Salt-stains, (A)..... 381
ROTH, ALBERT, Disposal of Tannery Waste..... 512

SANDER, A., Determining Sulphites in the Presence of Thiosulphates, (A) 240
SCHETTLER, G. A., Measurement of Leather, (A)..... 376
SCHMIDT, R., (see Appelius, W.).
SCHOLL, C., (see Bartow, E.).
SCHUBERT, ADOLF, (see Reed, H. C.).
SCHULTE, J. H., Sulphite-cellulose as Tanning Agent, (A)..... 335
SELTZER, J. M., Report of Committee on Extraction..... 467
SEYEWETZ, A., (see Meunier, L.).
SEYMOUR-JONES, A., Growth of Mould on Harness Leather..... 180
SINGH, PURAN, Nickel Tannates..... 186
SMALL, F. H., Extraction Thimble..... 32
SMALL, F. H., Report of Sulphite-cellulose Committee..... 36
SMITH, A. W., Nizhni Novgorod Fair, (A)..... 116
SMOOT, C. C., III, Sewage Disposal and the Use of Tannery Waste... 523
SODY, LOUIS, Sulphuric Acid in Leather, (A)..... 122
SOMMERHOFF, E. O., Solubilization of Phlobaphenes, (A)..... 200
SOMMERHOFF, E. O., Alcoholic Tannage, etc., (A)..... 200
SPIERS, C. W., Estimation of Tannin in Cider, (A)..... 373
SPRAGUE, F. O., Sole Leather Bleaching, (A)..... 496
STIASNY, E., Qualitative Differentiation of Vegetable Tannins..... 19
STIASNY, E., Tanning with Artificial Products..... 230
STIASNY, E., Value of Scientific Training for the Leather Manufacturer 386

TARSHIS, R. V., A Rapid Method of Chrome Analysis..... 258
TEAS, W. H., Interpretation of Tannery Analyses..... 52
THUAU, U. J., AND R. MADRU, Sulphuric Acid in Leather and Sulphited Extracts, (A) 380
TRAUBE, I., Tubing from Hardened Glue, (A)..... 191
TURNBULL, A., Pure Salt and its Value to the Leather Industry..... 412

VAN GIJN, J. L., The Heavy Leather Industry of Holland..... 410
VAN GIJN, J. L., AND H. VAN DER WAERDEN, Determination of Pentoses in Tanning Materials and Extracts..... 109
VAN TASSEL, E. D., JR., A New Emulsifying Agent..... 236
VEITCH, F. P., AND J. S. ROGERS, The Clarification of Leather Extracts for the Determination of Reducing Sugars..... 421

WILLIAMSON, C. G., Relation of Acidity to Yield, (A)..... 374
WILSON, J. A., (see McCandlish, Douglas).
WISDOM, ROY H., Estimation of Tanning Materials in Admixture.... 136
WISDOM, ROY H., Note on Comparative Analysis Report..... 174
WITHINSHAW, J. D., Leather Manufacture in China..... 397
WOOD, J. T., Further Notes on Enzyms..... 250
WOOD, J. T., Light Leather Liming Control..... 318
WOOD, J. T., Some Remarks on Liming..... 390

YOCUM, J. H., Imported Raw Vegetable Tanning Materials, (A)..... 241
YOCUM, J. H., Prevention of Salt Stains, (A)..... 242

Digitized by Google

INDEX OF SUBJECTS

Acid in Leather, Determination of Free Sulphuric,— Otto Kress..... 79
Sulphuric—, L. Sody, (A)..... 122
W. Moeller, (A) 122
M. Jalade, (A) 162
Estimation of Free Sulphuric—, J. Paessler, (A).. .....87, 243, 336
Sulphuric—, (A) 337
The Rehbein Method of Determining Free Sulphuric—, W. J. Kelley..... 340
and Sulphited Extracts, Sulphuric—, U. J. Thuau and R. Madru, (A)..... 380
Acidity of Leather, Determination of—, P. Nicolardot, (A)..... 377
Acidity to Yield, Relation of—, C. G. Williamson, (A)..... 374
A. L. C. A., Interrelation between the— and the National Association of Tanners, Cudworth Beye 97
Alcohol Tannage, W. Eitner, (A)..... 201
Alcoholic Tannage, E. O. Sommerhoff, (A)..... 200
Alum Tanning, Modern—, J. Jettmar, (A)..... 275
Aluminum, Applications of Active—: the "Alungallines," E. Kohn-Abrest 260
Analysis, Report of Committee on Comparative—, C. R. Delaney..... 70
Note on Comparative—, Report, R. H. Wisdom..... 174
of East India Leather, M. C. Lamb, (A)..... 375
Analyses, Interpretation of—, W. H. Teas..... 52
Contract—, Oma Carr 139
Anniversary of the Foundation of the German Tanning School, (A) 374
Annual Meeting, A. L. C. A., Tenth—..... 3
Eleventh— 500
Anthrax Disinfection, G. Abt, (A)..... 264

Bark Tans and Wood Tans, Distinction between—, B. Kohnstein, (A) 119
Bating with Oropon, (A)..... 160
Bleaching Sole Leather, F. O. Sprague, (A)..... 496
British Section, I. A. L. T. C.....64, 563

Carbonyl, Active—, and Tannage with Organic Substances, G. Powarnin, (A) 567
Carnauba Wax, C. Lüdecke, (A)..... 124
Cattle Industry in Paraguay, J. Frontanilla, (A)..... 164
Cattle in Argentina, H. W. Mumford, (A)..... 192
Cellulose Extracts, Investigation of—, J. Paessler, (A)..... 566
Chemical Annual, Van Nostrand's—, (book notice)..... 189
Chemical Reagents, their Purity and Tests, (book notice)..... 371
Chestnut Extracts, Contribution to the Knowledge of—, L. Pollak, (A) 571
China, Leather Manufacture in—, J. D. Withinshaw..... 397
Chrome Analysis, A Rapid Method of—, R. V. Tarshis..... 258
Soap in Chrome Leathers, G. Hugonin, (A)..... 379
Tanning, New Process of—, (A)..... 565
Chromium Determination, Methods of—, L. Balderston..... 255
in Leather, L. E. Levi and A. C. Orthmann 328
Clarification of Leather Extracts for the Determination of Reducing Sugars, F. P. Veitch and J. S. Rogers..... 421
Collodion in Leather Finishing, C. A. Higgins, (A)..... 374
Colloid's Lament, The—, E. Hendrick..... 248
Colloidal Tannins, M. C. Lamb..... 359

Digitized by Google

Color Measurement of Extracts, H. R. Procter 225
Methods of Fixing—, (A) 190
Testing, Discussion of Report on— 103
Valuation of Tanning Materials, H. C. Reed 170
G. A. Kerr 451
Contribution to the History of a New Industry, A. Muller-Jacobs 234
Council Meeting 13, 66, 384
Cutch, Charles Eachus, (A) 117

Danish Leather Industry, Max Ballin 408
Decolorizing Tanning Extracts, W. Hildt, (P) 125
Agent for Tanning Extracts, L. Pollak, (A) 271
Decolorization of Oils and Fats, (A) 418
Depilating, Notes on—, Allen Rogers 42
Process of—, O. Röhm, (P) 126
Depsides, Lichen-Substances and Tannins, E. Fischer 280
Abstract of the same 164
Dictionary, Leather Trades Technical—, F. Kohl, (book notice) 61
Dyestuff Situation in America, Allen Rogers 538

Emulsifying Agent, A New—, E. D. Van Tassel, Jr. 236
Enzyms, Further Notes on—, J. T. Wood 250
Evaporator and Dryer, A New Form of—, L. Balderston 442
Extraction of Tanning Materials in Copper and Glass, C. R. Oberfell and L. M. Richeson 28
Thimble for Use with the Teas Method, F. H. Small 32
Report of Committee on—, J. M. Seltzer 467

Fats, Chemistry and Analysis of—, for the Year 1913, W. Fahrion, (A) 333
Fat-liquor, Preparation of a—, (A) 417
Filipinos Adopting Occidental Foot-wear, J. F. Boomer, (A) 371
Filter Method of Tannin Analysis, L. Balderston 238
Forms, Standard—, for Reporting Analyses, W. K. Alsop 479
Forty Years Ago, H. R. Procter 354
French Section, I. A. L. T. C. 378

Gambier, Asahan, J. Paessler, (A) 168
Gelatin, The Equilibrium of Dilute Hydrochloric Acid and—, H. R. Procter 207
Goat Skins Tanned with the Hair, (A) 190
Grain, Tender—, and its Prevention, W. Eitner, (A) 122
Grease, Recovery of—, P. M. C. Armstrong 327
Guara, W. Eitner, (A) 241

Hardness in Natural Waters, Determination of—, C. Bahlmann, (A) 198
Hide, The Relation between the Green Salted Weight and White Weight of Various Portions of the—, F. A. Loveland 463
Hides, Classification of—, (A) 61
Neutral Inspection of—, (A) 62
Conservation of—, A. H. Lockwood, (A) 63
Method of Storing—, W. H. Allen, (P) 382
Brightening—, with Lactic Acid, (A) 417
Softening Dried—, (A) 418
and Skins, Second Report of the International Commission for the Preservation, Cure and Disinfection of—, (A) ... 416
Holland, The Heavy Leather Industry of—, J. L. Van Gijn 410
Hydrogenated Oils, Analytical Constants of—, Carleton Ellis 197

Digitized by Google

Industrial Chemistry and the Leather Industry, C. R. Oberfell..... 55
Insolubles, Determination of—, in the Analysis of Tanning Extracts, W. K. Alsop 465
Inspection of Hides, Neutral—, (A)..... 62
Interpretation of Tannery Analyses, W. H. Teas..... 52
Analytical Results, J. R. Blockey..... 362

Jerked Beef, South American Slaughterings for—, (A)..... 376

Kjeldahl Apparatus, A Compact—, H. G. Bennett..... 394

Larch, Bark of the German—, (A)..... 190
Lactic Acid, Method of Brightening Hides with—, (A)..... 417
Leaching, Laboratory Apparatus for— Experiments, L. Balderston and W. K. Alsop..... 484
Leather from Artificial Hide, W. Eitner, (A)..... 121
Iron Tanned—, J. Bystron, (P)..... 127
and Shoes in Asia Minor, (A)..... 191
Patent—, J. G. Ritter, (A)..... 191
Oak—, (discussion), (A)..... 194
Manufacture, Economical—, M. C. Lamb, (A)..... 242
Trades' Year Book, (book notice)..... 370
Analysis of East India—, M. C. Lamb, (A)..... 375
Relation between the "Feel" of— and its Appearance under the Microscope, R. F. Innes, (A)..... 374
Definition of Adulterated—, (A)..... 416
Manufacture in China, J. D. Withinshaw..... 397
Industry, The Heavy— of Holland, J. L. Van Gijn..... 410
The Danish—, Max Ballin..... 408
The Russian— 402
Lime, Hydrated—, H. E. Bachtenkircher, (A)..... 63
for Water Softening, E. Bartow and C. Scholl, (A)..... 198
Lime-Arsenic Paints, R. F. Innes, (A)..... 416
Liming Control, Light Leather—, J. T. Wood..... 318
Some Remarks on—, J. T. Wood..... 390

Mangrove, Detection of—, G. A. Kerr..... 25
Bark, Tanning Extracts from—, W. F. Doty, (A)..... 445
Measurement of Leather, G. A. Schettler, (A)..... 376
Melting Point of Stuffing Greases, P. M. C. Armstrong..... 326
Methods, Change in—, Leather Analysis..... 2
Proposed Changes in— 68, 249
Addition to— 130
Proposed Addition to— 130
Moellon Analysis, Report of Committee on— and Hard Greases, T. A. Faust 548
Mould on Harness Leather, A. Seymour-Jones..... 180

Nickel Tannates, Puran Singh..... 186
Nizhni Novgorod Fair, Alfred W. Smith, (A)..... 116

Oak, The Detection of— in Tanning Extracts and Leathers, J. S. Rogers 525
Oil Tannage, (A) 195
Oils, Proposed Provisional Method for Sulphonated—.....68, 170
Discussion of Report on—..... 102

Digitized by Google

Oils, Analytical Constants of Hydrogenated—, Carleton Ellis, (A).. 197
and Fats, Report of Committee on—, C. R. Oberfell..... 545

Pentose, Determination of— in Tanning Materials and Extracts, J. L. Van Gijn and H. Van der Waerden..... 109
Pentoses in Tanning Materials and the Detection of Mangrove, H. C. Reed and Adolf Schubert..... 131
Phlobaphenes, Solubilization of—, E. O. Sommerhoff, (A)..... 200
Power from Spent Tan, C. E. Parker, (A)..... 376
Preservation of Hides and Skins, (A)..... 338
President's Address, W. K. Alsop.....14, 500
Proposed Provisional Method for Sulphonated Oils..... 68
Proposed Changes in Methods..... 68

Quality or Quantity? J. J. Desmond..... 34
Quinones, Tanning Properties of—, L. Meunier and A. Seyewetz, (A) 379

Rendement, Low—, and its Cause, J. G. Ritter, (A)..... 199
Russian Leather Industry 402

Salt, Pure—, and its Value to the Leather Industry, A. Turnbull..... 412
Stains, (A) 167
Preventing—, (A) 241
Prevention of—, J. H. Yocum, (A)..... 242
G. Abt, (A) 272
Avoidance of—, C. Romana and G. Baldracco, (A).... 387
Sampling, Discussion of Report on—..... 88
School, Leather Trade—, at Madras, (A)..... 161
Sewage, Experiments on the Oxidation of—, without Filters, E. Ardern and W. T. Lookett, (A)..... 331
Disposal Work, Government Supervision of—, (A)..... 376
and the Use of Tannery Wastes, C. C. Smoot, III 523
Shoe Trade of Argentina, (A)..... 242
Skins, Analysis of Matter Adhering to Goat—, M. C. Lamb, (A).... 373
Soap for Fat-liquors, (A)..... 190
Sponges from Leather, (A)..... 372
Spruce Extract, Use of—, in Tanning, C. M. Proctor, (A)..... 242
Sugars, Clarification of Leather Extracts for the Determination of Reducing—, F. P. Veitch and J. S. Rogers..... 421
Sulphides in Lime Liquors, J. R. Blockey and P. V. Mehd..... 176
The Determination of Alkaline—, Douglas McCandlish and J. A. Wilson 203
Sulphite-cellulose, Report of Committee, F. H. Small..... 36
Extracts, Discussion of Report on—..... 106
Lye as a Tanning Agent and its Detection in Leather, W. Moeller, (A)..... 246
Blends, W. H. Dickerson..... 489
Lye as a Tanning Agent, J. H. Schulte, (A)..... 335
Paul Gulden, (A)..... 336
Use of Cinchonine for the Detection of—, W. Appelius and R. Schmidt, (A)..... 566
Sulphonated Fats, Waxes, etc., I. Levinstein, (P)..... 127
Sulphurous Acid in the Presence of Thiosulphates, Determining—, A. Sander, (A) 240
Surface Combustion, W. A. Bone, (A)..... 416

Tannage, (discussion), (A) 194

Digitized by Google

Tanners' Institute, Research Work by Students of—, (A)..... 332
Tannery Effluents and their Purification, J. Garcon, (A)..... 191
Purification of—, E. Rolants, (A)..... 195
Waste, Disposal of—, Albert Roth..... 512
Tannin Analysis, Filter Method of—, L. Balderston..... 238
in Chestnut Extracts, New Method for the Determination of—, L. Eglene, (A)..... 240
Bearers of South America, H. G. Cutler, (A)..... 242
Analysis, Further Progress in—, H. G. Bennett, (A)..... 243
Composition of—, L. F. Iljin, (A)..... 276
Constitution of—, A. Geake and M. Nierenstein, (A)....277, 445
in Cider, Estimation of—, C. W. Spiers, (A)..... 373
Tanning by Means of Fluorine and Chromium, (A)..... 190
Process, J. Y. Johnson, (P).....201, 447
with Artificial Products, E. Stiasny..... 230
Extracts, Distinguishing and Testing—, R. Laufmann, (A) 245
Skins, Compounds for—, L. Pollak, (P)..... 448
Process, Rapid—, (A) 418
Improvement in Rapid—, (A)..... 564
New Process of Chrome—, (A)..... 565
Material, Max Hönig, (P)..... 126
Materials in Admixture, Roy H. Wisdom..... 136
New—, (A) 159
Production of—, in German Colonies, (A)..... 165
Imported Raw Vegetable—, J. H. Yocum, (A)... 241
of Paraguay, J. Frontanilla, (A)..... 277
Some New Tests for—, H. G. Bennett..... 436
Tannins, Qualitative Differentiation of Vegetable—, E. Stiasny..... 19
Some Recent Advances in the Chemistry of the—, M. Nierenstein 227
Colloidal—, M. C. Lamb..... 359
Tubing from Hardened Glue, I. Traube, (A)..... 191

Ulmo Bark, Use of the So-called—, (A)..... 445
Understanding between the Tannery Chemist and the Tannery Superintendent, What can We do to Promote a Better—, W. R. Cox 509
Unsaponifiable Constituents of Natural and Hardened Fats, J. Marcusson and G. Meyerheim, (A)..... 334

Value of Scientific Training to the Leather Manufacturer, E. Stiasny 386

Warble Problem, The Ox—, S. Fraser, (A)..... 446
Water and its Purification for Tanning Purposes, M. F. Corin..... 143
Purification and the Permutit Process, E. E. Basch, (A)..... 158
Waters, Determination of Hardness in Natural—, C. Bahlmann, (A) 198
Wattle Bark in South Africa, Government Inspection of—, (A)..... 338

Yellow, A Study in—, C. A. McNeil, (A)..... 243

ARTICLES FROM OTHER JOURNALS

(Page numbers without titles refer to abstracts.)

Berichte 276, 277
Bourse aux Cuirs de Liége.....164, 277
Bulletin of the Imperial Institute.....159, 338
Bulletin Société d'Encouragement pour l'Industrie National..191, 264, 272

Digitized by Google

Chemical Engineer 63
Chemiker Zeitung 158, 191
Collegium... 119, 164, 200, 243, 271, 272, 373, 374, 381, 416, 445, 566, 567, 571
Estimation of Free Sulphuric Acid in Leather 87
Determination of Pentose in Tanning Materials 109
The Estimation of Sulphides in Lime Liquors 176
Further Notes on Enzyms 250
Light Leather Liming Control 318
A Compact Kjeldahl Apparatus 394
Conceria 189, 190, 417, 418, 445
Consular and Trade Reports 116, 161, 191, 371, 376, 445
Der Gerber 121, 122, 168, 191, 199, 201, 241
Gerber-Courier 122, 195
Hide and Leather 117, 242, 446
Journal of the American Chemical Society—
Synthesis of Depsides, Lichen-substances and Tannins 280
Journal of Industrial and Engineering Chemistry 197, 198
Journal of the Royal Society of Arts 416
Journal of the Society of Chemical Industry 331, 374, 416
Nickel Tannates 186
La Halle aux Cuirs 162, 194, 195, 377
Researches on the Applications of Active Aluminum 260
Leather Trades' Review 61, 64, 160, 372, 374, 563
Growth of Mould on Harness Leather 180
Leather Trades' Year Book 374, 375, 376
Forty Years Ago 354
Colloidal Tannins 359
The Practical Interpretation of Analytical Results 362
The Value of Scientific Training to the Leather Manufacturer .. 386
Some Remarks on Liming 390
The Prospects of Leather Manufacture in China 397
The Russian Leather Industry 402
The Danish Leather Industry 408
The Heavy Leather Industry of Holland 410
Pure Salt and its Value to the Leather Industry 412
Leather Manufacturer 564
Leather World—
Some Recent Advances in the Chemistry of the Tannins 227
Le Cuir 167, 194, 378, 379, 380
Ledertechnische Rundschau 122, 246, 275, 335, 336
Le Marche des Cuirs 195
Shoe and Leather Reporter 241, 242, 243, 496, 565
Color Measurements of Extracts 225
Tanning with Artificial Products 230
Some New Tests for Tanning Materials 436
Shoe and Leather Weekly 62, 63, 192
Technikum 124, 165, 167, 337
Transactions of the Chemical Society (British)—
Equilibrium of Dilute Hydrochloric Acid and Gelatin 207
Zeitschrift für angewandte Chemie 240, 333, 334

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. IX JANUARY, 1914 No. 1

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1914, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VEITCH, } . . . Past Presidents

OFFICERS, 1913-'14

PRESIDENT—W. K. ALSOP, Ridgway, Pa.
VICE-PRESIDENT—C. W. NORRIS, 80 South Street, New York, N. Y.
SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.
COUNCIL—A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y.
LLOYD BALDERSTON, Ridgway, Pa.
C. R. OBERFELL, Harrisonburg, Va.
T. A. FAUST, 323 Academy Street, Newark, N. J.

ELECTIONS.

ACTIVE

Magnus F. Corin, 511 Hansberry St., Germantown, Philadelphia, Pa.
Robert L. Laffenander, Pratt Institute, Brooklyn, N. Y.

ASSOCIATE.

William H. Gardner, Basic City, Virginia.
Lee Howard Lincoln, Port Allegany, Pa.
George F. Rumpf, 1213 Venango St., Philadelphia, Pa.

BOUND VOLUMES OF THE JOURNAL.

Copies of Volume VIII of the JOURNAL, for the year 1913, are now ready, bound in cloth or half morocco, uniform with previous volumes. Price $6 per volume, delivered. Copies of

Digitized by Google

all previous volumes are also on hand. Bound volumes will be sent in exchange for sets of unbound numbers at the rate of $1.20 per volume, delivered. Missing numbers will be supplied at 25 cents each. Unbound numbers for exchange should be well packed and sent to the Manager at Ridgway, Pa., expressage prepaid at the "printed matter" rate.

CHANGE IN METHODS, LEATHER ANALYSIS.
(Glucose Determination.)

The vote on the proposed changes was as follows:—Total vote, 42; necessary for adoption, 28; for adoption, 37; for rejection, 5. The change is therefore adopted, and will become effective upon the publication of this notice in the JOURNAL.

H. C. REED, *Secretary.*

The revised method is as follows:

SOLUTIONS:

Copper Sulphate.

Dissolve 34.639 g. of $CuSO_4.5H_2O$ in distilled water and dilute to 500 cc. Filter through asbestos.

Alkaline Tartrate Solution.

Dissolve 173 g. of Rochelle salt and 50 g. NaOH in water and dilute to 500 cc. Allow to stand two days and filter through asbestos.

Normal Lead Acetate Solution.

Prepare a saturated solution of normal lead acetate.

Determination of Glucose.[9]

Place 200 cc. of leather extract of analytical strength in a ½-liter flask, add 25 cc. of a saturated solution of normal lead acetate, shake frequently (5-10 min.), and filter. (The funnels and beakers must be kept covered to prevent evaporation.) Add to the filtrate an excess of solid potassium oxalate. Mix frequently for 15 min. and filter, returning the filtrate until clear.

[9] The rate of heating of the Bunsen burner used should be regulated before sugar determinations are started. This is best done by adjusting the burner so as to bring 25 cc. copper soln. + 25 cc. alk. tartrate soln. + 50 cc. H_2O in a 400 cc. beaker to 100° C. in exactly four minutes.

Digitized by Google

Pipette 150 cc. of this filtrate into a 600 cc. Erlenmeyer flask, add 5 cc. of concentrated HCl and boil under a reflux condenser for 2 hrs. Cool, neutralize (place a small piece of litmus paper in the flask) with anhydrous sodium carbonate, transfer to a 200 cc. graduated flask and make to volume. Filter through a double filter. (The filtrate must be clear.) Determine the dextrose in the solution immediately.

Place 25 cc. of the copper solution and 25 cc. of the alkaline tartrate solution in a 400 cc. beaker. Add 50 cc. of the clarified and neutralized solution above mentioned and heat to boiling in *exactly* 4 *min.* and boil for 2 min. Filter immediately without diluting, *through asbestos,*[10] wash thoroughly with hot water, then with alcohol, and finally with ether; dry for half an hour in water oven and weigh as cuprous oxide, determine the amount of dextrose by the use of Munson and Walker's table (Bull. 107, Rev. Bu. of Chem., p. 243) and report in percentage on leather.

TENTH ANNUAL MEETING.

The tenth annual convention of the American Leather Chemists Association was held at the Hotel Traymore, Atlantic City, N. J., beginning on Thursday, Dec. 4. The Association was called to order by the President, W. K. Alsop, Secretary H. C. Reed being also at the table. The meetings were held in the sun parlor on the top floor of the hotel. The following is a nearly complete list of those who attended:

C. C. Smoot, III; H. B. Van Dyne, George L. Adams, W. T. Buchanan, F. H. Small, W. H. Dickerson, Sig. Saxe, George A. Kerr, Charles M. Kernahan, Henry W. Healy, A. O. Beardmore, George W. Daugherty, Edward D. Van Tassel, Jr., Charles R. Delaney, L. M. Richeson, J. S. Robeson, H. T. Wilson, F. O. Sprague, R. W. Griffith, Edgar A. Prosser George D. McLaughlin, Lee H. Lincoln, Thomas Blackadder, Cudworth Beye, Thomas A. Faust, F. S. Havens, Reinhold A. Lang, P. S. Tilden, Roy L.

[10] The finely divided, long-fibered asbestos to be used in the glucose determination should be digested with HNO_3, washed, then digested with NaOH and washed. When gooch filters are prepared, they should be washed with boiling Fehling's solution, then with HNO_3. The mats thus prepared can be used for a long time.

Digitized by Google

Wisdom, M. F. Corin, Charles R. Oberfell, M. F. Nichols, Walter R. Snell, F. P. Veitch, Neale Ransom, J. S. Rogers, Henry H. Hurt, Edwin J. Haley, L. Balderston, J. Edgar Rhoads, W. H. Dickerson, B. S. Agnew, P. R. Smith, Oskar Reithof, Harry W. Smith, John Helfrich, W. H. Teas, Allen Rogers, Louis E. Levi, George L. Rumpf, W. P. Maxwell, C. M. Morrison, C. W. Norris, K. G. Mackenzie, R. C. Jacobsen, W. H. Gardner, J. G. Brown, J. S. Harman, Edward J. White, F. A. Loveland.

The opening address was delivered by President Alsop. (The text of the address follows this synopsis of the meeting.)

H. C. Reed then read the Secretary's and Treasurer's reports.

Secretary's Report, 1913

Total Active Members, December 1st, 1913		133
Total Associate Members, December 1st, 1913		141
Total Membership December 1st, 1913		274
Active Members elected during the year	21	
Associate Members elected during the year	17	
Total additions		38
Active Members resigned during the year	9	
Associate Members resigned during the year	14	
Associate Members died during the year	1	
Total losses		24
Net gain		14
Total Membership December 1st, 1912	260	
Net gain during 1913	14	
Total Membership December 1st, 1913	274	

Deaths, Horton Johnson.

Treasurer's Report, 1913

General Account

Balance, December 1st, 1912		$ 793.31
Annual dues	$1,170.12	
Contingent expenses (not used)	125.00	
Procter Laboratory fund	478.50	
Interest	7.10	1,780.72
		$2,574.03

Digitized by Google

Disbursements

Annual meeting expenses	322.75	
Council meeting expenses	163.60	
Committee expenses	76.40	
Clerical expenses	250.00	
Printing, stamps, envelopes, telegrams, expressage	315.70	
Contingent expenses (as above)	125.00	
	$1,253.45	
To JOURNAL account	135.93	1,389.38
Balance December 1st, 1913		$1,184.65

Journal Account

Receipts

Advertisers	$1,326.40	
For JOURNALS	61.25	
For bound volumes	46.50	$1,434.15

Disbursements

JOURNALS December 1912, to November 1913	$1,033.00	
Abstracts and Translations	219.95	
Reprints	98.85	
Editor's expenses	141.53	
Subscriptions	30.50	
Bound volumes	21.75	
Index	24.50	$1,570.08
JOURNAL deficit Nov. 30th 1912, to Dec. 1st, 1913.		$ 135.93

Recapitulation

Balance December 1st, 1912	$ 793.31	
Receipts	3,214.87	$4,008.18
Expenditures		2,823.53
Balance December 1st, 1913		$1,184.65
Due from advertisers	$293.34	
Unpaid dues	210.00	

The President then called for the report of the committee on oils and fats. The Chairman, C. R. Oberfell, presented the report, which was published in the December Journal. The discussion which followed this report will appear in a later issue.

The chairman of the committee on color testing was not present, and the report was presented by F. H. Small. The tests made by the collaborators were exhibited. This report was also printed in the December Journal. A rather long discussion followed the reading of the report, an abstract of which will be published later.

Digitized by Google

At the last annual meeting the Secretary was requested to communicate with Schleicher and Schull with reference to the complaints which have been made in regard to the quality of their filter paper, No. 590. His report was now called for, and is as follows:

New York, Dec. 1st, 1913.

REPORT ON No. 590, S. & S., 15 CM. FILTER PAPERS.

Reporting on the No. 590 Filter Papers, I quote the following correspondence with the manufacturers, Carl Schleicher & Schull, Dueren, Germany, (January 15th 1913).

"At the recent Annual Conference of the American Leather Chemists Association held at Washington, D. C., I as Secretary of the Association, was requested to communicate directly with you to ascertain if something could not be done to obtain a more uniform and better quality filter paper, than has been furnished us recently. The paper prescribed by the A. L. C. A., method for tannin analysis in the filtration of tannin solutions, is your No. 590 S. & S., 15 cm., grade, and the faults we have to find with it are of varied character. Frequently whole packages of the filters are so absolutely rotten as to make it almost impossible to pleat without tearing. With an expensive paper such as the No. 590, this means a considerable actual money loss, and our method states that the papers shall be pleated. Another feature that causes trouble, is the lack of uniformity in the thickness and weight. All filter paper absorbs tannin to a greater or less degree, and the heavier the paper the greater the tannin absorption. This variation in weight necessitates the discarding of many filters. The variation in thickness is not confined to separate filters, but may be observed in one and the same paper, one portion being considerably thicker than another.

Will you kindly take this matter up with me as Secretary of the A. L. C. A., with the view of bettering the existing conditions? Certainly the reputation of your filter papers will suffer greatly if something is not done. What we desire is a paper that will fold without breaking, but not a heavy paper. The lighter the paper, the better, so long as it will not break. At the same time, we desire no other grade of paper than the No. 590, as the official method specifies its use."

Digitized by Google

Schleicher & Schull replied on the 14th of February, as follows:—

"We have carefully studied the contents of your favor of the 15th ultimo, and are sorry that you have to complain as to the quality of our chemically pure filters, No. 590—15 cm. Our filters No. 590 represent a hand made article and you will understand that as it is almost impossible to turn out one sheet in the same thickness of another, small variations will therefore be entirely unavoidable.

After all the reference samples we have kept back from former supplies show that the filters are partly a little too thin, which of course, must be avoided in the future. We are sending you separately samples of our present stock, which we hope will answer your wishes.

You may rely upon us, that it will be our utmost endeavor to satisfy you, and do not hesitate to believe that we shall be successful, and all filters No. 590—15 cm., we send to the United States in the future will be specially selected."

H. C. REED.

Mr. Reed said further that for a time he got very good filters, but that recently he had found the same difficulty, the papers being liable to break in folding. The sample package sent by S. and S. were excellent. T. A. Faust recalled the suggestion made last year that an attempt be made to arrange with Schleicher and Schull for a special line of filters made for the Association and handled by some member. C. W. Norris said that the manufacturers might be willing to furnish a special selection of filters to the Secretary through their American agents. Mr. Norris reported having to discard in some instances as many as 40 per cent. of the filters in a package.

F. H. Small next presented the report of the committee on sulphite-cellulose, extracts which appears elsewhere in the present number.

The second session convened at about 3 o'clock in the afternoon, Dec. 4. George A. Kerr presented a paper on the detection of mangrove. This paper is published in this issue of the JOURNAL.

Digitized by Google

L. M. Richeson then read a paper on the extraction of tanning materials in copper and glass, which is printed in this number.

F. H. Small read "Remarks concerning an extraction thimble," which will also be found in this number.

President Alsop next called for a report from the committee on comparative analysis, C. R. Delaney, Chairman. Mr. Delaney presented a partial report, the work having been completed so recently that there had not been time to tabulate results.

F. P. Veitch, Chairman of the committee on free sulphuric acid in leather, was next called on. He gave a brief verbal report, and then read the paper on the same topic which had been written by Dr. Otto Kress. This, with the discussion which followed, will appear later.

S. Saxe was next called upon. He read a correspondence with Professor Procter in reference to methods of reporting the analyses of materials containing sulphite-cellulose extract. This was followed by a long discussion. The letters and discussion will be published in a future number.

The third session was held on Friday morning, Dec. 6. The first matter was the report of the committee on sampling, presented by C. W. Norris. This report had been printed in the December Journal. An additional proposal in regard to the sampling of solid extracts was submitted, to be known as proposal C. It is as follows: On units of weight of 50,000 or less, the number of packages to be sampled shall be represented by 3 per cent. of the weight. A spirited discussion followed the presentation of this report. A synopsis of the discussion will be printed later.

M. F. Corin read a paper on the Purification of Water, which was followed by a long discussion. Both paper and discussion will appear in a future number of the JOURNAL.

F. A. Loveland read J. J. Desmond's paper, "Quality or Quantity," which is published in the present time.

W. H. Dickerson presented notes on some experiments with sulphite-cellulose extracts, which will be published later.

At the afternoon session on Friday, Cudworth Beye addressed the Association on the interrelation between the A. L. C. A. and

Digitized by Google

the National Association of Tanners. Mr. Beye is the Executive Secretary of the N. A. T.

Much discussion followed this address, in the course of which a resolution was adopted in favor of holding the next annual meeting of the A. L. C. A. at Chicago at the time of the meeting of the N. A. T., and devoting as much time as may be necessary to the discussion of topics of interest to the associate members. The paper and an abstract of the discussion will appear in a future issue.

Dr. Allen Rogers now read his paper on "Depilating Methods," which is printed in this number.

The paper by F. P. Veitch and J. S. Rogers on the Clarification of Leather Extracts for the Determination of Reducing Sugar was read by the former. This paper and the discussion following will be printed later.

H. C. Reed, Chairman of the committee on Procter Laboratory fund, reported about $500 subscribed. It was decided to issue a third appeal to the members, asking for small and prompt subscriptions from all who had not already responded.

F. P. Veitch, Chairman of the committee on tannery waste, stated that but little had been done in the course of the year on the subject. He asked that those interested send samples of tannery effluents to the Leather Laboraory. Further discussion on the utilization of tannery wastes was carried on by H. W. Healy, F. P. Veitch and others. An abstract of this will appear in a future number.

On Saturday morning, Dec. 6, C. R. Oberfell read his paper on "Industrial Chemistry and the Leather Industry," which appears in this number.

W. H. Teas then gave an address on the Interpretation of Tannery Analyses, which is published in this issue.

The President appointed F. P. Veitch and H. H. Hurt as tellers to count the votes which had been cast in the election for members of Council. While the count was in progress, R. C. Jacobsen was invited to speak. He said

"Mr. President and Gentlemen: This invitation is as unexpected as it is pleasant. It is always a great pleasure to me to talk to the trade. As a general rule, I am told, I talk

Digitized by Google

too much to them, but these discussions during the past two days make me feel that by degrees we are all of us striving to achieve perfection. It may be we are a long way from it, but it calls to my mind an experience I remember in regard to Sam Jones, the celebrated evangelist. He was down in Atlanta and was talking about perfection, and he said, "Has anybody ever seen a perfect man? If so, stand up." Of course nobody arose. There is no perfect man—except perhaps in this Association. Then he said, "Is there a perfect woman? Are there any perfect women in the world? Does anybody know of a perfect woman?" A little woman stood up in the audience. "Ah! sister, have you seen or heard of a perfect woman? Now you will tell us something." "Well," the little old woman piped up, "I've heard a good deal about her, but I've never seen her. She was my husband's first wife."

Well, gentlemen, I can look back to the time when there was no Chemists' Association; when tanners were throwing millions of dollars of material away in their tanneries. I don't know whether you remember Dr. H. E. Sturcky or not. I think he was here before your Association was formed. I remember when he came at the invitation of Jackson Schultz and began analyzing "spent" tan bark for tanners, and found they were leaving half of the tannic acid in the bark; and I believe that that was the first time that the tanners really were stirred up in regard to the great need of the chemist.

Now I did not prepare any paper to-day. I did not expect to speak, but it always seems to me when I am in the company of an Association like this that it proves to be a great source of stimulation. In listening to your papers—of course there are a great many hard words used, some perhaps you don't understand yourselves, but they are all good words—it struck me that at your future meetings you might possibly improve by having one day devoted say to tannery problems, having the tanners here. Now you are going to meet, as I understand, next year with the National Tanners Association and this may result in expanding the usefulness of your Association.

Then it struck me also, if I may take the liberty of making the suggestion, that the question of chemical engineering might be

Digitized by Google

taken up. That is a very important point. Probably your Council has discussed this.

I think while we are here this morning something might be said in regard to a sesearch station. I refer to the one in Vienna so long and so ably directed by Wilhelm Eitner. I don't know exactly what steps could be taken. These things have to be talked about before practice follows; but it does seem as though something might be done so that some members, or some one member of your Association, might possibly be placed in position where entire attention could be given to original research.

I have been surprised—of course I am not a chemist; I am simply a hard-working newspaper man—but I have been surprised at hearing chemists mention the possibilities they can see in perfecting the leather industry. I was talking with a leather machinery man the other day. He insisted that their machines were far from perfection, but that progress is being made. It does seem as though steps might be taken some of these days to arrange for our industrial chemists to have time to get away from the bread-and-butter effort, the same as they have to-day in the domain of medicine and surgery. And sometimes I think if our big tanners were approached, particularly those who are approaching old age and not in very good health, if it were polite to suggest it to them, that they might think of endowing a school of original research. Something might come of this, because it is only by having opportunity to give your time and leisure to these problems that big things can be done.

We are going along, but it is simply part and parcel of our daily bread. And in regard to this question of going ahead, a man in a train the other day was telling me a little story. I do not know how veracious it is, because you do not always hear truth in the smoking compartment of a Pullman car; but he spoke about a man out in Dakota who was very much bothered by the loss of his sheep. The coyotes kept taking them away; and he heard of a wonderful dog about 5 miles distant that might be obtained for $10. Well, he decided after a while that it was cheaper to pay $10 for a good dog than to continue losing sheep, so he bought the dog. All his neighbors heard about it, as they always do in these country places, and of course they were very much interested in the result. Well, the old man was

Digitized by Google

down in the store in the little town a short time later and somebody was speaking about the dog, and he said, yes, he had him; he had him; and he was asked, "What is your experience with him?" Well," he said, "the other morning mighty early I heard a terrible noise in the yard outside, and I looked out, and there I saw the biggest coyote I have ever seen—the biggest coyote; and there was Pete, my dog," he said, "and they were running at full speed. I says, 'Go it, Pete! Go it, Pete!'" The old man stopped, and a little fellow from behind the stove piped out, "Did he ketch him?" The old man replied, "Catch hell! Pete was ahead."

Well, gentlemen, I am not going to take any more of your time. I am very much obliged for this opportunity. You know in our paper, *Hide and Leather,* we have always been very friendly to the chemist. We know what the chemist can do, and I think, gentlemen, it is sometimes absolutely pathetic to hear an occasional tanner declare he has no use for the chemist. I have seen the time—and I think you will agree with me—when it was almost a joke for a tanner to take chemistry seriously. The chemist was regarded as a joke; and I think the fault was on both sides. Of course this is bringing up ancient history, but I can look back farther in memory possibly than some of you—but the chemist was too enthusiastic and the tanner was too hopeful, and I have seen some terrible mistakes made; but that is the inevitable price that is always paid for progress. To-day it is a great source of gratification to see the chemists coming into their own and rising higher and higher and getting better remuneration, while at the same time the tanners themselves have benefited greatly. They feel and recognize what the chemist is doing for them.

Gentlemen, I thank you very much for your attention, and it seems to me that possibly here this morning something further might be said on the question of this research work.

I want to say a few words about the Seventh National Shoe and Leather Fair we shall hold in Mechanics Building, Boston, next July, the week of July 8-15. If your Association would like a space there, or anything we can possibly do, to serve as headquarters, we shall be very glad to furnish it without any charge

Digitized by Google

whatsoever. I presume that it is up to your Council to decide how you would like to accept that invitation. If it does not prove practical to accept it, that is all right, our feelings won't be hurt; but we feel a very great admiration for and interest in your Association, and if you can see your way to having headquarters at the Fair, without any charge whatsoever, we will provide the necessary signs for you and furniture, and it might be opportunity for another meeting of your Association.

I thank you, gentlemen."

The election resulted in the choice of T. A. Faust and C. R. Oberfell as members of council for two years. (A paper sent by Dr. Stiasny arrived too late to be presented. It is printed in this number.)

COUNCIL MEETING.

At a meeting of the Council of the American Leather Chemists' Association, held at Hotel Traymore, Atlantic City, N. J. December 6th, 1913, there were present Messrs. Oberfell, Balderston, Reed, Alsop, Norris and Faust.

Two active and three associate members were elected.

Mr. Reed read a letter from the National Tanners' Association on the subject of the Advisory Committee of the Tanners' Institute, and upon motion, duly seconded it was resolved that the two members of the A. L. C. A. on that committee be re-appointed, viz. Messrs. Alsop and Yocum.

The matter of the contribution to the Procter Research Laboratory was discussed and Mr. Reed was directed to endeavor to get all contributions in by January 1st. The matter of making the contribution up to a round sum out of the Association's treasury was left for discussion until the Council meeting to be held early in January.

The meeting adjourned to January 3rd, 1914, the place of meeting to be decided later.

Digitized by Google

PRESIDENT'S ADDRESS.*

By W. K. Alsop.

I shall confine my remarks in general to an expression of opinion as to some of the affairs of the Association.

Four of our Annual Meetings have been held in Washington, two in Chicago and one each in New York, Boston and St. Louis. At the time of the first meeting, held in St. Louis, the total membership of the Association was 19. At this, our tenth, it is 274. This increase in membership is very gratifying, comprising as it does, practically all those engaged in leather chemistry in this country and so large a number of those sufficiently interested in the aims and work of the Association to become affiliated with it.

According to the By-Laws, the objects of this Association are:

a. To investigate the methods of analysis of tanning materials, and all other materials connected with the manfacture of leather, with intent of perfecting or improving such methods.

b. To publish all papers and information on matters above mentioned in such manner as may seem advisable.

c. To do all other things in any way connected with the accomplishment of the objects above mentioned.

These things we have been doing in a more or less thorough manner for 10 years. The method for the analysis of tanning materials, which occupied so much of our time at first, has not been altered very materially for a number of years, the most radical change being that made this year. It appears unlikely, in the light of our present knowledge, that important changes will be necessary in the near future, except possibly, to provide for the analysis of new materials that may be introduced, perhaps synthetic tannins, of which the Neradol D of Stiasny may be the forerunner, may be also sulphite cellulose extracts, which seem to have afforded an opportunity for a considerable display of eloquence at our meetings lately.

We have a fairly satisfactory method for leather analysis, with the exception of the determination of free acid in leather and the

* *A. L. C. A.*, Convention Atlantic City, Dec. 4, 1913.

Digitized by Google

important matter of sampling: that the latter is a difficult matter to satisfactorily settle may be shown by the following incident. A a meeting of the International Association of Leather Trade Chemists, at which I was present, an attempt was made to agree upon a method of analysis. The first, and only, thing discussed was methods of sampling, and finally the whole matter had to be referred to a Committee. Perhaps we have wisely left this matter to the last, although at first glance it may seem rather peculiar. Probably it would be better to have something in the method as to manner of stating the results of leather analysis, a subject often brought up, but one on which no action has been taken.

Our methods of oil and fat analysis are not in very satisfactory shape, but a good start has been made which should lead to outlining such methods as may seem to be desirable.

The methods of sampling have been revised this year by a Committee throughly competent to deal with the subject and the report will be presented to this meeting.

We still have no satisfactory method for estimating the color valuation of tanning materials. A great deal of experimenting has been done, both individually and in collaboration, but without arriving at results sufficiently uniform to make it advisable to adopt an official method. It may be that we have something to learn from the International Association in this matter. Would it not be better to drop our present provisional method and adopt one more in line with the general procedure? Determination of acidity of tanning liquors is still a perplexing problem. The method is probably as good a general one as we have, but it leaves much to be desired. The results have not the value they should have owing to the fact that the determination of the total acidity, with one indicator, at least, does not necessarily show the plumping value of the liquor, due to the different acids which may be present, and the influence exerted upon plumping, by these acids, of mineral salts and tannins and non-tannins. The subject at present seems to be one requiring individual research rather than committee work.

The determination and estimation of tanning materials in mixtures is another problem that is not satisfactorily solved as

Digitized by Google

yet. The increasing use of blends of different materials makes it a matter more and more desirable of solution and in the past few years a great deal of research work has been expended upon the problem, especially abroad.

We have no methods dealing with analyses in connection with beam house procedure, and comparatively little has been published by American members of the Association dealing with this subject. Dr. Parker says: "The leather chemist would find in the lime yard of the tannery, problems of greater financial and scientific interest than disputing over ¼ or ½ per cent. differences in the analyses of tanning extracts." Have we as an Association given this matter the attention that it deserves?

Several years ago we had committees working to compile methods for testing acids used in the tannery and for the past two years have had a committee on the analysis of lactic acid. No action has been taken, however. Neither have we methods for materials used in chrome leather manufacture, bichromate, thiosulphate, chrome liquors, etc.; also numerous other materials used in leather manufacture, bleaching materials, bleach liquors, lime, etc. Should we not have methods for these materials, not necessarily "Official" nor even "Provisional" if that also implies too much of an abligation on the part of members to use them. Could not our pamphlet of methods be made of much more value to the leather chemist? It would be largely a matter of compilation and not entail the experimenting and research that our other methods required.

We have published each year a pamphlet containing our Official and Provisional Methods and also issue a monthly journal now in its eighth year. As I happen to be editor of this JOURNAL, perhaps I am in a better position to speak of some features in reference to it than most of you.

There is no question but that the JOURNAL is an important factor in the work of the Association and that it has had a marked influence upon the membership. It is duty of the editors to issue as good a JOURNAL as they can with the material procurable and the means at hand. But surely a great part of the responsibility rests on the members of the Association on

Digitized by Google

whom they must mostly rely for original articles, whether chemical, technical or of general interest to the trade.

From January to December of this year it contained 28 original articles from 18 members of the Association and 7 of these have been reports by chairmen of committees; also the papers by 8 members reprinted from other journals or pamphlets. I will leave it to you whether you have done your duty in this respect, bearing in mind that 18 from a membership of 274 have contributed. It is an interesting and gratifying fact to note that 2 of the more important papers published this year have come to us unsolicited.

We received an interesting paper recently from one of our members. He wrote me in reference to it as follows:—"As you say you are in immediate need of an article, I am sending you one—which may do to fill space, though it is not the sort of stuff you usually publish and would appeal to practical men rather than chemists." Rather rough on chemists, but as he is one, we will pass it without further comment.

If any of you have a similar delusion, let me assure you that we need articles of interest to "practical" men as well as those—I can think of no satisfactory ending to that sentence so will pass on. We endeavor to give you abstracts of articles of interest as well as circumstances permit, and for this purpose obtain, either by exchange or purchase, 25 periodicals from various countries as follows:—

United States	6
Great Britian	5
France	4
Belgium	1
Germany & Austria	7
Hungary	1
Italy	1

It appears to be the custom in continental Europe to send an article to all the papers one can think of, so the same paper is sometimes appearing in several periodicals at once. Frequently, there are almost unending discussions which seem hardly worth while following. Also, occasionally, articles appear apparently written to prove certain things, without due regard to scientific or other facts, so that the material available for our purpose is not as large as one might suppose. Let me ask you to help us

Digitized by Google

not only to maintain the JOURNAL in the position it occupies, but to make it of more value to both active and associate members.

From what has been said, if my opinion as to the status of our affairs at all agrees with yours, there seems to be still some work for us to do, both individually and collectively, in respect to perfecting our methods of analysis. But is this all we should attempt?

Your President, in his address at the second annual meeting, stated, in effect, that as this was the sole aim of our Association we should have no difficulty in working together in unison as no problems encroaching into the field of manufacturing were involved. In another presidential address a few years later, the opinion was advanced that we should do more than this and endeavor to work as a body on some of the problems more directly connected with manufacture. This same idea was largely the theme of Dr. Parker's address at the last convention of the International Association. Has not the status of the chemist changed somewhat in the past 10 years? It is a fact that the character of our meetings has changed somewhat and for the better. We usually have one or more addresses from manufacturers and other papers dealing with subjects not connected directly with methods of analysis. More manufacturers are becoming interested in our meetings, although the number who attend as yet is small.

Do not our committees on Disposal of Tannery Waste and Salt Stains indicate that we are gradually being drawn into work somewhat outside the narrow limits as set down in the By-Laws?

We are to have an address from the Executive Secretary of the National Association of Tanners on the Interrelation of the Associations. If we should be brought into a closer relation with that body, would not this tend to hasten the day when the expressed aims of our Association will be broadened, must be, in my opinion, if we are not to retrograde. After all, is not this matter largely in the hands of the manufacturers? Almost all of the active members, either directly or indirectly, are employed by them, and the scope of our work would seem to be dependent, to a great extent, upon the measure of their co-operation and the aims of their associations.

Digitized by Google

FURTHER CONTRIBUTIONS TO THE QUALITATIVE DIFFERENTIATION OF VEGETABLE TANNINS.

By E. Stiasny.

Since the author's last publication (Collegium 1912, page 483) only a few papers have been published dealing with the above subject. By far the most important, is the paper of R. Lauffmann (Collegium 1913, page 10.) Lauffmann suggests the precipitation of tannin solutions with a mixture of ammonium molybdate, and ammonium chloride, and he finds that different tannins show distinct and considerable differences in the so-called molybdenum figure.[1] It is especially the behavior of quebracho and mangrove which requires our attention, because a method for distinguishing between these two and for detecting mangrove in mixtures with quebracho extract, both natural and chemically treated, is badly needed by the leather trades chemists as well as by the tanning extract manufacturers.

Lauffmann found in untreated quebracho extract Mo-figures varying from 28 to 37. In sulphited quebracho extract figures varying from 5 to 37,[2] and in mangrove extracts figures from 120 to 130, whilst the sulphited mangrove extract was only slightly lower, 111.3.

Mixtures of quebracho extract (sulphited or not) with mangrove gave figures which were in very good concordance with those calculated from the components. The practical conclusion was therefore drawn, that quebracho extracts, containing no pyrogallol tans (formaldehyde test) and no wood pulp (aniline test) may be regarded as adulterated with mangrove if the Mo figure is found to be higher than 30 to 40. In the case of strongly sulphited extracts the lower limit (30) can be taken.[3]

The author, in conjunction with Mr. C. D. Wilkinson, has tested the above reaction in a considerable number of cases, and

[1] Mo figure is the weight of the precipitate obtained from 100 milligram tannin; for further details see Lauffmann's original paper (English abstract. *Collegium*, 1913, page 119 (Abst. this J., 1913, p. 55.)

[2] Quebracho extract which was chemically treated without the use of sulphites gave figures similar to those of untreated quebracho extract.

[3] Mr. Lauffmann, in a private communication suggests as the result of a large number of determinations a limit of 16 for sulphited quebracho extracts.

Digitized by Google

the results obtained are in good concordance with Lauffmann's figures. It may be stated that this test will prove in all probability a very valuable one, especially if used together with other tests mentioned in my previous papers. The great advantage of Lauffmann's test compared with all previous tests, lies in the fact that mangrove may be detected even in mixture with sulphited quebracho extract; but the variations of the Mo figure obtained for quebracho and sulphited quebracho are such as to vitiate to some extent the practical utility of the test.

Sulphited quebracho extract yields values for the Mo figure varying from 5 to 37, the lower values being obtained by strongly sulphited extracts; whereas lightly sulphited extracts would yield the higher values. Moreover, Mr. Wilkinson found in a few cases Mo figures of practically zero, whilst Mr. Lauffmann mentions a strongly sulphited extract with a Mo figure of 21.3. It is therefore possible to adulterate a strongly sulphited quebracho extract (say with Mo fig. 5) with 20 per cent. mangrove (Mo fig. 125) without reaching the limit of 30.[4]

This example shows the shortcomings of Lauffmann's test: and it was desired to find an improved method of carrying out the reaction. The principle of this proposed improvement is to treat the extract before determining the Mo figure in such a way so as to lower the Mo figure of quebracho to less than 5, but at the same time to leave the Mo figure of mangrove higher than 100. All differences caused by a previous treatment of the extracts should disappear by such a process. The method employed consisted of sulphiting under different conditions as follows:—

(*a*) 20 grms. liquid extract heated with 5 grms. $NaHSO_3$ (30 per cent.) + 0.75 grms. Na_2CO_3 on the water bath for 12 hours.

(*b*) As in (*a*), but with subsequent addition of 12.8 cc. N/2 HCl.

(*c*) As in (*a*), then re-sulphited with 10 grms. $NaHSO_3$ (30 per cent.) in autoclave for three hours at 110°-120° C.

[4] Taking 16 as a limit for the Mo figure of sulphited quebracho extracts, the percentage of mangrove which might escape detection in the above example would amount to 9 per cent.

Digitized by Google

(*d*) 20 grms. liquid extract heated with 5 grms. $NaHSO_3$ (30 per cent.) in the autoclave for three hours at 110°-120° C.

The Mo figures obtained are given in the following tables.

	a.	b.	c.	d.
Quebracho extract	0.0	0.5	0.0	9.0
				15.4
				8.5
Mangrove extract	0.0	17.8	0.0	104.8
				71.9

These results can be summarized by the following statement:— Strong methods of sulphiting which bring down the Mo figure of quebracho extracts (previously sulphited or not) to zero or nearly zero, also diminish the Mo figure for mangrove so considerably (in some cases even to zero) that no distinction between mangrove and quebracho can be based upon these figures. Milder methods of sulphiting diminish the Mo figure for quebracho insufficiently, and diminish the Mo figure of Mangrove so much that no improvement on the original method of Lauffmann is obtained.

The negative results, though not promising, are communicated with the idea of directing the attention of colleagues to the possibility of other methods of sulphiting or to other treatment which may lead to satisfactory differences in the Mo figure.

Although our present knowledge of the qualitative behavior of vegetable tannins is still very incomplete, an attempt may be allowed to make use of the various tests and observations published in this and in some previous papers to bring these tests into the form of a scheme for practical use in the laboratory.

The following proposed scheme is open for improvement, and it is hoped that it will soon be amended and extended, and if necessary, corrected. It has however been found useful in the author's laboratory, and students have in almost every case been able to identify a single tannin by the use of this scheme.

The scheme divides the tanins in three main groups and each of these groups in two sub-divisions. As far as possible confirmation tests have been suggested in support of the group tests in order to avoid errors. The formaldehyde test is made first; and the reaction may proceed in three different ways, according to which the tannin is placed into Groups I, II, or III.

Digitized by Google

Group I. Complete precipitate: the filtrate gives neither gelatin test nor iron test.

Tests for confirmation; bromine test (precipitate) and acetic acid-lead acetate test (no precipitate).

Group II. No precipitation during fifteen minutes boiling.

Test for confirmation: bromine test (no precipitate); ammonium sulphide test (precipitate).

Group III. Considerable precipitate during boiling, but distinct iron test of the filtrate.

To Group I belong: quebracho, mangrove, ulmo, gambier, pinebark, hemlock, mimosa, malet.

To Group II belong: oak-wood, chestnut-wood, valonia, myrobalans.

To Group III belong: oakbark, pistacia lentiscus, sumac, divi-divi, agarobilla, teri, bablah, galls.

Having found to which group the tannin belongs, the following tests are made in each group:—

Further testing of Group I.—The ammonium-sulphide test allows a subdivision, in so far as no precipitate is obtained with quebracho, mangrove, ulmo, gambier, pinebark, hemlock (Group Ia) while a precipitate is shown by minosa and malet (Group Ib).

Group Ia is also characterized by the green coloration produced with iron alum.

Group Ib gives a bluish violet with iron alum.

The further way of identifying the tannin in Ia or Ib, demands the carrying out of all the tests mentioned in previous papers and summarized in Table II. This table also contains the gallic acid value of one grm. of the tannin and the proportion of tans to non-tans in the tanning material. The Mo figures found by Mr. Lauffmann are also given in the table.

Further testing of Group II.—The acetic acid-lead acetate test allows a subdivision, as no coloration is given by the addition of iron alum to the filtrate of the lead precipitation, in the case of oak-wood and valonia (Group IIa); while a more or less distinct violet coloration is obtained with myrobalans and chestnut (Group IIb).

Digitized by Google

TABLE I.

50 cc. tannin solution (0.4 per cent.) boiled with 25 cc. of the HCHO-HCl mixture for 30 minutes, thoroughly cooled and filtered.

Complete precipitate: Filtrate + iron alum + sodium acetate: no violet coloration.	No precipitate after 15 minutes boiling.	Considerable precipitate after 15 minutes boiling; deep violet color ation of the filtrate + iron alum + sodium acetate.
GROUP I.	GROUP II.	GROUP III.
Confirming tests: + bromine: precipitate. + acetic acid + lead acetate: no precipitate.	Confirming tests: + bromine: no precipitate. Ammonium-sulphide test: precipitate.	
25 cc. tannin solution (2.5 per cent.) + ammonium-sulphide test.	5 cc. tannin solution (0.4 per cent.) + acetic acid lead-acetate test. The filtrate of the precipitate gives + iron alum.	5 cc. tannin solution (0.4 per cent.) + bromine test.

No precipitate.	Precipitate.	No coloration.	Violet coloration.	Precipitate.	No precipitate.
GROUP Ia.	GROUP Ib.	GROUP IIa.	GROUP IIb.	GROUP IIIa.	GROUP IIIb.
Confirming tests: + iron alum.					
green	bluish violet	Oakwood	Chestnut	Oakbark	Sumac
Quebracho	Mimosa	Valonia	Myrobs	Pistacia	Divi
Mangrove	Malet				Algarobilla
Ulmo					Galls
Gambier					Bablah
Pine-bark					Teri
Hemlock					

Digitized by Google

TABLE II.

	Formaldehyde-test		Bromine-test	Ammonium-sulphide test	Lead-acetate test. Filtrate + NaOH	Acetic acid + lead acetate test		Ethyl-acetate figure	Alcohol figure	Gallic acid value of 1 gm. tannin (See *Collegium*, 1909, p. 191)	Tans / Non-tans	Molybdenum figure (Lauffmann)
	During 15 min. boiling	Filtrate + iron alum + sodium acetate					Filtrate + iron alum					
Quebracho . .	pp.	No coloration	pp.	No pp.	Yellowish	No pp.	Green	70-80	0-5	0.59	8.0-10.0	25-40
Sulphited-quebracho . .	pp.	No coloration	pp.	No pp.	Yellowish	No pp. (but $PbSO_4$)	Green	0-70	0-5	0.59	depends on the method of sulphiting	0-20
Mangrove . . .	pp.	No coloration	pp.	No pp.	Colorless	No pp.	Green	0-5	0-5	0.68	2.5- 4.0	100-135
Ulmo	pp.	No coloration	pp.	No pp.	Yellowish	No pp.	Green	70-80	0-5	. . .	8.0-10.0	42
Gambier . . .	pp.	No coloration	pp.	No pp.	. . . .	No pp.	Green	50-65	5-10	0.56	1.2- 1.5	0-19
Mimosa	pp.	No coloration	pp.	pp.	Colorless	No pp.	Deep bluish violet	30-40	0-5	0.53	2 0- 3.0	110-130
Oakbark . . .	pp.	Violet	pp.	pp.	Colorless	pp.	. . . .	12	17	. . .	1.0- 1.5	135
Hemlock . . .	pp.	No coloration	pp.	pp. (after standing overnight)	Yellowish	No pp.	Green	18	9	. . .	1.0- 2.0	65-85
Pistacia	pp.	Deep bluish violet	pp.	pp.	Yellow	pp.	Green & violet	3	29	. . .	. .	. . .
Chestnut . . .	No pp.	Deep bluish violet	No pp.	pp.	Colorless	pp.	Very faint violet	0-16	10-20	0.56-0.66	2.0- 3-5	180-225
Oakwood . . .	No pp.	Deep bluish violet	No pp.	pp.	Colorless	pp.	Colorless	0-12	20-30	0.5 -0.56	1.0- 2.0	175-210
Myrobalans. .	pp.	Deep bluish violet	No pp.	pp.	Colorless	pp.	Violet	30-50	0-15	0.55-0.60	1.5- 2.5	80-140
Sumac	pp.	Deep bluish violet	No pp.	pp.	Yellow	pp.	Violet	40-60	5-20	0.65-0.69	1.5- 1.8	125-155
Valonia	turbid	Deep bluish violet	No pp	pp.	Colorless	pp.	Colorless	5-15	20-40	0.55-0.63	2.0- 3.0	222
Divi-divi . . .	turbid	Deep bluish violet	No pp.	pp.	Colorless	pp.	Violet	30-50	0-10	. . .	2	. . .
Algarobilla . .	turbid	Deep bluish violet	No pp.	pp.	Colorless	pp.	Violet	50-60	0-5	. . .	2	. . .
Wood pulp . .	No pp.	No coloration	No pp.	Not characteristic	Deep yellow	No pp.	Colorless	0-5	30-70	0.09-0.14	0.75	. . .

Digitized by Google

The further testing in these groups is done with the help of Table II.

Further testing of Group III.—The bromine test allows a subdivision, a precipitate being obtained with oakbark and pistacia lentiscus (Group IIIa) while sumac, didi-divi, algarobilla, etc., give no precipitate (Group IIIb).

Here again, all tests given in Table II must be applied to identify the tannin; and this is less easily done in this than in the other groups.

The Table I gives the scheme of qualitative analysis of vegetable tannins.

THE DETECTION OF MANGROVE IN ADMIXTURE WITH OTHER TANNING MATERIALS.

By Geo. A. Kerr.

Without having read all that has been written relative to methods designed to identify tannins of two or more derivatives in a mixture of commercial tanning materials, I am of the impression that much of the work in this direction has dealt in efforts to discover distinctive reactions of the tannins themselves, rather than attempting to take advantage of any peculiar characteristic of their accompanying non-tannin components (the test for chlorides in the case of mangrove being an exception), although it will probably be found that some of the published qualitative tests owe whatever value they may posses to reactions of the non-tannis, and not to the tannin itself, as may be supposed.

During the course of research work in non-tannins, it was observed that those of certain materials gave reactions which, when properly interpreted, would serve to indentify them under most conditions to be met with in commercial products. The most notable of these reactions so far observed is that of mangrove, and it is a qualitative test for its presence in any appreciable quantity in other tanning materials I am now submitting.

When quebracho, mangrove, chestnut, chestnut oak bark and hemlock extracts are distilled with hydrochloric acid, they yield more or less furfural and other analogous products, which

Digitized by Google

give distinctive color reactions when a solution of phloroglucin is added. This distinction is not confined to the solution, but is also noticeable in the precipitated phloroglucid.

Quebracho, chestnut, chestnut oak bark and hemlock are not distinguishable from each other, as all of them yield a similar color development. Upon adding the phloroglucin, the color is first a brilliant yellow, gradually becoming a bright green and finally assuming a bluish tint as the precipitate forms, this latter becoming a dense black. The distillate from mangrove, however, gives quite a different color reaction. Beginning with an orange yellow, it developes to a deep orange, and the precipitate is of a buff color instead of black.

In the materials enumerated above, mangrove is detected by the modification of the intense green color of the solution by the orange of the mangrove, and the mixture of the buff colored precipitate with the black. In mixtures containing as low as 5 per cent. of mangrove, the green color is modified to a distinct olive, but from this point upward the olive becomes yellower until at 50 per cent. the green color due to any of the other materials is completely dominated by the strong orange of the mangrove. When the mangrove in a mixture is so low as to render the color reaction uncertain, a microscopic examination of the precipitate with a low power objective will define the mixture of the two precipitates.

I will try to demonstrate that here. The distillates I have here are about a month old and I do not know if I will get as good a color reaction as I might with fresh ones. This (indicating a bottle of distillate) is a pure mangrove, and here you can almost notice the color of the distillate. (Adds the phloroglucin.) Now this (indicating another bottle) is pure quebracho. (Adds the phloroglucin).

This (indicating) is a 10 per cent. mangrove. (Adds the reagent.) This (indicating) is 50 per cent. mangrove. (Adds the reagent.) It usually takes 5 minutes for these quebrachos to develop.

Noting the difference of the precipitated phloroglucid, and assuming the distillates are products of the non-tannins, some

Digitized by Google

possibility of developing this method quantitatively suggests itself. Thus, if the yield of phloroglucid depends upon the proportion of certain of the non-tannins present, it would seem that mangrove should give a much greater precipitate than quebracho; therefore, if the quantity of phloroglucid produced by each of these two materials can be determined gravimetrically, the proportions of a mixture could be obtained with a fair degree of accuracy. Failure to accomplish this, however, is not difficult to anticipate for, unless the yield of furfural given by the various materials is constant within well defined limits, and such constant do not overlap, confusion would ensue.

Quantitatively, the color reaction is not without value, as close approximations of the mangrove contents may be made by comparison with the distillates of known mixtures compounded in the laboratory from pure materials.

In this connection, Mr. H. C. Reed, at my request, last June sent four samples, marked "A," "B," "C" and "D," respectively, but of unknown composition as to their contents of quebracho and mangrove, with the object of giving the test a trial. Mr. Reed now holds the key to these samples, and I shall ask him to enlighten us as to the accuracy of the results, it being borne in mind that a qualitative test only was anticipated. "A," "B" and "D" contain mangrove in quantity, but "C" is pure quebracho.

MR. REED, "That is correct."

Without having compared them with known mixtures, I should say that, quantitatively, they ran about as follows:—"A" 30 per cent., "B" 10 per cent. and "D" 20 per cent. mangrove.

MR. REED: "'A,' 45 per cent. 'B' 15 per cent. and 'D,' 35 per cent."

The reagents necessary for the test are a 12 per cent. solution of hydrochloric acid and pure phloroglucin.

The procedure is as follows:

One hundred cc. of 12 per cent. HCl solution are placed in 250 cc. Erlenmeyer flask, and to this is added 2 grams of the tanning material to be tested, finely powdered, if dry, or an equivalent quantity, if the material is in liquid form.

The flask should be well shaken upon the addition of the

Digitized by Google

material and a few pieces of freshly ignited pumice stone added to prevent caking. It is then connected to an ordinary spiral glass condenser, set vertically, under the discharge of which is placed a graduated cylinder or flask to receive the distillate, which must be filtered by placing a small funnel and filter in the receiver. Distillation is then proceeded with at the rate of about 30 cc. every ten minutes, 30 cc. of the HCl solution being added through a thistle tube as each 30 cc. of distillate comes over, this being continued until 300 cc. have been taken off.

In case the test is to be merely qualitative, the first 50 cc. of distillate may be discarded, as it contains little if any of the products of distillation. The next 150 cc. is sufficient for the test. To test the distillate, place 100 cc. in a beaker 2 inches in diameter and add 8 cc. of the phloroglucin solution, which has been made by dissolving 0.25 gram in 25 cc. of the 12 per cent. HCl solution. Stir a few moments and observe the color development, which reaches its maximum in about 5 minutes, although it is sufficiently permanent to distinguish differences, for hours.

A COMPARISON OF THE EXTRACTION OF VEGETABLE MATERIALS CONTAINING TANNIN IN COPPER AND GLASS.*

By C. R. Oberfell and L. M. Richeson.

Under the heading "Extraction" in the recently adopted Official Methods of Analysis of this Association there appears a clause to the effect that the material of the boiling flask must be inert to the percolate, meaning the tannin infusion. In support of their position in adding this clause the Revision Committee state that "it has been shown[1] that copper flasks have a decidedly detrimental effect on tannin solutions upon continued boiling." From another source it has been intimated also that there is perhaps a loss of tannin due to the copper material of the extractor proper.

In the course of a line of research work we wished to definitely settle these two points in order to eliminate a possible error re-

* Read at the *A. L. C. A.* Convention, Atlantic City, Dec. 4, 1913.

[1] This Journal vol. II. page 274.

Digitized by Google

sulting from a destruction of tannin in this manner. Accordingly a series of experiments were planned the results of which are found in Tables I and II.

The apparatus employed was made in one case entirely of glass; condenser, extractor and boiling flask, and in the other case of copper. The extractors being a duplication of what is called the Teas type, or an arrangement to conform strictly with the requirements of the Official Methods.

A variety of materials were selected and in each case were extracted and analyzed at the same time and in accordance with the officially prescribed procedure.

Table I, new materials, includes chestnut-oak, black oak and hemlock barks, sumac, valonia and divi-divi. The barks being subjected to reflux extraction involving continuous boiling for 14 hours after the removal of the stronger fractions, while the sumac, valonia, and divi-divi were extracted by percolation and the effect of the material of the extractor alone would be involved.

TABLE I.—NEW MATERIALS.

	Total solids	Soluble solids	Insolubles	Non-tannin	Tannin	Tannin diff.
No. 988-9—Chestnut oak bark.						
(Glass)	23.01	20.98	2.03	8.38	12.60	—
(Copper)	24.41	21.57	2.84	8.74	12.83	0.23
No. 994-5—Chestnut oak bark.						
(Glass)	22.19	20.43	1.76	8.07	12.36	—
(Copper)	23.10	20.47	2.63	8.11	12.36	0.00
No. 1014-5—Chestnut oak bark.						
(Glass)	24.41	20.99	3.42	8.34	12.65	0.10
(Copper)	23.68	20.86	2.82	8.31	12.55	—
No. 1031-2—Black oak bark.						
(Glass)	16.63	15.61	1.02	6.48	9.15	—
(Copper)	17.18	15.88	1.30	6.65	9.23	0.08
No. 1028-9 -Hemlock bark.						
(Glass)	20.71	16.48	4.23	5.92	10.56	0.19
(Copper)	20.10	16.18	3.92	5.81	10.37	—
No. 1012-3—Sumac.						
(Glass)	39.67	36.75	2.92	20.44	16.31	0.21
(Copper)	41.58	37.63	3.95	21.53	16.10	—
No. 1018-9—Divi-Divi.						
(Glass)	74.53	72.58	1.95	25.25	47.33	—
(Copper)	74.25	72.68	1.57	25.32	47.36	0.03
No. 1009-10—Valonia.						
(Glass)	63.04	60.38	2.66	20.53	39.85	—
(Copper)	64.79	62.31	2.48	22.40	39.91	0.06

Digitized by Google

It was noticed early in the work that due to the difference in the heat conductivity of the glass and copper it was difficult to obtain infusions with relatively the same amount of total soluble material. This was guarded against as much as possible by insulating the glass extractor with asbestos paper and only small differences will be noticed following the first extractions. In the case of the valonia we were unable to obtain comparative soluble solids.

TABLE II.—SPENT MATERIALS.

	Total solids	Soluble solids	Insoluble	Non-tannin	Tannin	Tannin diff.
No. 993-6—Spent bark.						
(Glass)	3.37	2.85	0.52	1.84	1.01	—
(Copper)	4.32	3.47	0.85	2.24	1.23	0.22
No. 1000-1—Spent bark.						
(Glass)	4.08	3.78	0.30	2.58	1.20	—
(Copper)	4.61	4.37	0.24	3.04	1.33	0.13
No. 1006-7—Spent bark.						
(Glass)	5.09	4.46	0.63	2.84	1.62	—
(Copper)	5.01	4.56	0.45	2.93	1.63	0.01
No. 1042-3—Spent bark.						
(Glass)	5.47	4.35	1.12	2.79	1.56	0.16
(Copper)	4.76	4.25	0.51	2.85	1.40	—
No. 1046-7—Spent bark.						
(Glass)	4.71	4.24	0.47	2.51	1.73	—
(Copper)	5.15	4.59	0.56	2.85	1.74	0.01
No. 1048-9—Spent bark.						
(Glass)	7.36	6.29	1.07	3.74	2.55	0.15
(Copper)	7.19	6.02	1.17	3.62	2.40	—
No. 1003-4—Spent wood.						
(Glass)	6.00	4.72	1.28	2.80	1.92	0.14
(Copper)	5.38	4.67	0.71	2.89	1.78	—
No. 1038-9—Spent wood.						
(Glass)	7.59	6.55	1.04	4.76	1.79	0.16
(Copper)	7.06	6.32	0.74	4.69	1.63	—
No. 1040-1—Spent wood.						
(Glass)	5.92	5.35	0.57	3.93	1.42	0.17
(Copper)	5.36	5.02	0.34	3.77	1.25	—

The differences obtained in the tannin content on both new and spent materials are well within the limits of accuracy of the method and indicate that the copper flask and extractor have no appreciable effect. In the case of new materials the average difference per determination is 0.0125 per cent. glass over the

Digitized by Google

copper and with spent materials the average difference per determination is 0.046 per cent. copper over the glass. This is shown in Table III.

TABLE III.—NEW MATERIALS.

Sample Number	Per cent. diff. copper over glass	Per cent. diff. glass over copper
988-9	0.23	—
994-5	0.00	0.00
1014-5	—	0.10
1031-2	0.08	—
1028-9	—	0.19
1012-3	—	0.21
1018-9	0.03	—
1009-10	0.06	—
	0.40	0.50
Average difference per determination	0.0125 per cent.	
SPENT MATERIALS.		
993-6	0.22	—
1000-1	0.13	—
1006-7	0.01	—
1042-3	—	0.16
1046-7	0.01	—
1048-9	—	0.15
1003-4	—	0.14
1038-9	—	0.16
1040-1	—	0.17
	0.37	0.78
Average difference per determination	0.046 per cent.	

The only comparative work which we have on the relative effect of glass and copper is Reed's experiments in the report of the Extraction of Tanning Materials Committee in 1907[1]. Reed obtained more tannin when using glass boiling flasks but likewise the soluble solids were higher indicating that more heat had been applied and more material extracted. At the same time the method Reed used was continuous extraction and in this report he states. "It is possible that the same action takes place in a proportional degree in the weak solution obtained in the continuous extraction process *after* removal of the stronger fractions, but if so, its effect upon the ultimate result is but slight."

Taking this into consideration along with the results we

[1] This Journal, Vol. II, pages 239-80.

Digitized by Google

obtained it seems safe to say that glass offers no advantage, in that it has a destructive action, over copper in the extraction of tanning materials according to the present Official Methods.

AN EXTRACTION THIMBLE FOR USE WITH THE TEAS' METHOD.*

By F. H. Small.

The usual method of charging an extractor of the Teas' type with tanning material preparatory to the extracting of the same is to insert in the extractor a perforated porcelain plate supported a short distance above the bottom of the barrel of the extractor,—cover this plate with a layer of absorbent cotton, then pour in the material to be extracted. This is a somewhat bothersome procedure and there is always some uncertainty as to the efficiency of the cotton layer in preventing the passage of fine dust into the percolate.

With the idea of finding a more convenient method of charging the extractor and one insuring against the passage of dust into the percolate, experiments have been carried on in this laboratory, using as containers for the charge alundum thimbles kindly furnished by the Norton Co. The preliminary experimental work showed the following to be requisites to successful operation of these thimbles; sufficient porosity to permit the solvent to pass through more rapidly than delivered from the condenser,—this prevents flooding; the upper portion (⅔ works well) made impermeable to the solvent,— this prevents the solvent from passing out through the thimble in preference to passing down through the charge. In addition it is desirable that the thimble fit the extractor barrel as snugly as is consistent with easy entering and removal and the condenser must have a center drip tube so that the condensed solvent will be delivered into the thimble.

Thimbles satisfying the above conditions have been in use in this laboratory for nearly 2 months with comfort and success. The material to be extracted may be weighed directly in the tared thimble; and if several extractions are to be made, the thimbles in a stand may be successively filled when they need

* Read at the *A. L. C. A.* Convention, Atlantic City, Dec. 4, 1913.

Digitized by Google

merely to be slipped into the extractors. All danger of fine dust passing into the percolate is avoided. The thimbles are easily cleaned. After shaking out the extracted residue, drawing hot water through the thimble in the opposite direction to which the percolate runs will clean the thimble satisfactorily in short order. This cleaning is readily accomplished by inserting a one-hole rubber stopper snugly in the open end of the thimble, connecting this to an aspirator by a rubber tube, and a glass tube passing through the hole of the stopper, then immersing the whole thimble in a pail of hot water.

Extraction of small charges with the thimble, as against the perforated plate and cotton show only the usual experimental variations; with large charges the extraction is more complete with the thimble. I ascribe this to the fact that the tops of the extractors in common use in this laboratory had not center drip and the condensed water largely ran down the walls of the extractor instead of distributing itself evenly over the upper surface of the material being extracted. Specimen results on new and spent oak barks are as follows:

SPENT BARK.

	No. 1		No. 2		No. 3		No. 4	
	Perforated plate and cotton	Thimble	Perforated plate and cotton	Thimble	Perforated plate	Thimble	Perforated plate	Thimble
Total solids ..	9.73	10.05	9.02	9.37	8.66	8.93	8.72	9.21
Soluble solids	8.08	8.26	7.35	7.73	7.10	7.37	7.42	7.83
Non-tannin ..	3.64	3.79	3.39	3.00	3.22	3.46	3.32	3.61
Tannin	4.44	4.47	3.96	4.23	3.88	3.91	4.10	4.22
Insolubles ...	1.65	1.79	1.67	1.64	1.56	1.56	1.30	1.38

NEW BARK.

	No. 1		No. 2		No. 3	
	Perforated plate and cotton	Thimble	Perforated plate and cotton	Thimble	Perforated plate and cotton	Thimble
Total solids..	24.15	23.87	22.08	22.17	24.70	24.44
Soluble solids	20.75	20.75	19.30	19.47	21.02	20.82
Non-tannin..	8.63	8.54	7.97	7.95	8.24	8.21
Tannin.....	12.12	12.21	11.33	11.52	12.78	12.61
Insolubles ...	3.40	3.12	2.78	2.70	3.68	3.62

Similar thimbles are convenient for leather extractions, and other like purposes, it being practicable to dry and weigh the leather in the thimble without removal.

Digitized by Google

QUALITY OR QUANTITY.*

By J. J. Desmond.

Two years ago at Washington I urged you to give more thought and attention to hides which constituted by far the largest percentage of the tanners raw material.

The conservation of hides has been important in the past; it is vastly more so now when hides cost more than they ever did in the history of our trade. Their value now, is illustrated by a southern tanner who telegraphed a Chicago packer to send him a few hides by parcel post, for which he was sending a carload of money that day. How cheap hides were relatively when I first was connected with the tanning industry may be inferred from a remark made to me about that time by an old sole leather tanner from the Jackson Shultz yards at Wilcox. He was telling me of a most unusually stingy neighbor and exclaimed—"Why he is so close that he would skin a louse for his hide and tallow." That may have seemed close in those days when hides were cheap, but now even the skin of a louse would look valuable to a tanner.

By reason of this enormous cost the conservation of the hide to the utmost is of first importance, and by conservation, I mean as much the proper care and condition up to the time it reaches the beam house of the tannery, as such care and skill in the processes, as will make the finest and most serviceable leather at the lowest possible cost.

For years tanners have been hammered relentlessly for lower prices by leather buyers, who seemed to make price, not quality, the first essential. The result was that many tanners were tempted to take the "easiest way" and make cheap leather by filling it with anything that would add weight. They furnished quantity not quality. Without condoning the weakness of those tanners who used weighting material, I believe that the chemists and others who taught them, were equally culpable.

But that is of the past. The shoe manufacturer, speaking generally, is to-day willing to pay for a good article and anxious to get it. This being true, it is clearly the duty and should be the pleasure of the tanners to make the best possible product that

* Read at the *A. L. C. A.* Convention, Atlantic City, Dec. 5, 1913.

Digitized by Google

can be made by combining hides and tanning materials. We owe it to the shoe manufacturer to give him the utmost value, so that he in turn, can make a shoe worth the price he must ask for it. In this connection, I venture the prediction that in 5 years the popular priced shoe will sell for considerably more per pair, unless of course, substitution or panic should radically change the normal course of values.

Now, what constitutes real value in leather? Being a sole leather tanner I can not speak authoritatively on upper leather. I should say generally speaking, that the essentials of a shoe upper, named in the order of their desirability, were—tensile strength, pliability, and appearance. In sole leather, the first and by long odds the most essential quality is wear; after that pliable solidity and appearance.

To get the hide into the condition where it will give the most wear, it is essential to get the fibers as nearly vertical as possible, so that the wear will come on the ends, the same as the bristles in a brush. In order to make these fibers stand on end it is necessary to fill in between them with a soluble material, which uniting with the hide substance, becomes insoluble. This theory carried to a conclusion would make a perfect piece of sole leather. To put soluble materials into leather, which do not unite with the hide substance, or to apply insolubles to flesh or grain as some foreign tanners do, is adulteration, pure and simple. On the other hand, anything that will unite with the hide or tend to make and keep the fibers of the leather on end, or to preserve the leather, is legitimate and desirable tanning material.

If the spongy part of the hide like the belly, could be distended and filled with real tanning materials, you would have just as good a piece of leather as you have in the bend. The belly fiber is longer and naturally lies flatter,—more nearly horizontal than vertical.

The reason for the unusual wear of chrome sole in general lies in the fact that the mineral tanning tends to contract the fiber and in this way "stand it on end" in the same way that raw hide stretches when wet and rapidly contracts as it dries.

While on this question of adulteration, I feel warranted in speaking of the adulteration of extracts. It is not generally

Digitized by Google

known outside of the tanning trade, that a good deal of so-called adulterated leather, is adulterated because made from compounded extracts. When the maker, mixer or dispenser of adulterated extract foists his product on a tanner, he is compounding a felony on the human race—at least that part of it which wears shoes.

In conclusion, I want to ask the co-operation of you gentlemen, in the elimination of adulteration in any form, hides, extracts, leather.

For years foreign leather buyers looked to American leather for something cheap. That situation is changing. Let us cooperate to so change it that American leather will be the synonym for quality. There is no part of our individual business in which I take more pride than in the fact that foreign manufacturers pay us as much or a little more for our product than they pay for their own tannages. I think this is pardonable pride, for it is a striking evidence of quality. There is vastly more satisfaction and gratification in the production of a car of quality product than in a trainload of quantity product, and in the long run more profit.

REPORT OF THE COMMITTEE ON SULPHITE-CELLULOSE.*

By F. H. Small.

During the year which has elapsed since our last meeting the literature pertaining to sulphite-cellulose extracts has been enriched by various contributions, the majority of which have related to the use of this material in the tanning process. A few have had to do with methods of estimating qualitatively or quantitatively materials of this sort in admixture with regular tanning materials.

Eitner, in der Gerber Nos. 923-924; pps. 43-4, 57-9 mentions the relationship of the analysis figures as assisting in the detection and estimation of sulphite-cellulose, remarking that a high non-tannin and sometimes a high ash go with the presence of sulphite-cellulose material. Levi and Orthmann in their paper No. 3, on the analysis of the Tannins (Journal A. L. C. A.—April

* Read at the *A. L. C. A.* Convention, Atlantic City, Dec. 4, 1913.

Digitized by Google

1913, pps. 161-164) give data showing that whereas reagent No. 33 apparently precipitates largely the tannin in an extract, it fails almost completely to react with sulphite-cellulose materials, and so affords a means of estimating the amount of sulphite-cellulose extract in admixture. Monnet in the Collegium No. 517—pps. 224-225 gives data showing the possibility of different interpretations of the data afforded by the Procter-Hirst reaction in different laboratories, several operators reporting the presence of sulphite-cellulose material and others the absence in one and the same extract. Jedlicka (Collegium No. 518—pps. 317-319) in reply calls attention to the necessity of following exactly the prescriptions of the test as laid down in the original paper, if significant results are to be obtained. He further states that various pure Slavonian extracts do respond to the test, but the amount of S. C. material shown is so slight as to be of no commercial importance. He concludes that any extract may be designated free from added S. C. material if, when subjected to the P. H. test, it does not give a flocculent ppt. after two hours' standing. Jedlicka adds that S. C. extracts show a high sugar content and that the addition of such to a tannin extract results in raising its sugar value above normal. The question at issue in these latter papers —namely, the accuracy and delicacy of the Procter-Hirst reaction was the one that the Council requested should be given special attention by your Committee, the further sugestion being made that other confirmatory reactions were much to be desired.

During the year the Procter-Hirst reaction has been carefully tested by various members of the committee, and they report as follows:

MR. R. H. WISDOM:—"Insofar as the Procter-Hirst test is concerned, I have tested it under many and varying conditions during the past year with perfect success even in as small proportion as 5 per cent. This test has covered a considerable range of tanning materials, and I cannot endorse the test too highly."

MR. H. C. REED:—"The Procter-Hirst reaction has been tested very carefully in this laboratory and we find it capable of detecting when sulphite-cellulose is present in admixture of tanning extracts to the extent of from 2 to 3 per cent. We have yet

Digitized by Google

to test an extract, known to be a pure vegetable tanning extract, that gave the Procter-Hirst reaction."

DR. LLOYD BALDERSTON :—"I have examined 7 straight extracts and about 60 mixtures by the Procter-Hirst method, and give herewith a summary of my results.

Ordinary quebracho, straight, no ppt. even after standing 24 hours.
98 per cent. Q, 2 per cent. S. C., marked ppt. showing clearly in a few minutes.
95 per cent. Q, 5 per cent. S. C., larger ppt. settled to bottom.
90 per cent. Q, 10 per cent. S. C., still more ppt. partly settling and partly rising to the top of the solution.
80 per cent. Q, 20 per cent. S. C., ppt. larger than the last, nearly all rising.
70 per cent. Q, 30 per cent. S. C., ppt. still larger, most to the top.
60 per cent. Q, 40 per cent. S. C., ppt. still larger, mostly to top.
50 per cent. Q, 50 per cent. S. C., ppt. still larger, mostly to the bottom.
40 per cent. Q, 60 per cent. S. C., less ppt. than the last, all at the top.
30 per cent. Q, 70 per cent. S. C., still less, nearly all at top.
20 per cent. Q, 80 per cent. S. C., still smaller ppt., about like that from 80 per cent. Q and 20 per cent. S. C.
10 per cent. Q, 90 per cent. S. C., about the same as the last.

All the solutions of quebracho and sulphite-cellulose extract containing from 2 to 50 per cent. of the latter were cloudy at all temperatures, while those having from 60 to 90 per cent. were clear in all temperatures down to 20°. The mixed extracts (50 per cent. solids) were increasingly thick with larger percentages of sulphite-cellulose up to 50 per cent., and this mixture would not flow at 20° C. The mixture having 60 per cent. S. C. was quite liquid at 20° as also those with higher proportions. All these mixtures were made up on the basis of tanning substance present. That is, a 10 to 90 mixture does not mean 10 per cent. of one 50 per cent. solids extract, and 90 per cent. of another, but that 10 per cent. of the tanning matter present is of one sort and 90 per cent. of the other.

Straight hemlock extract, no ppt., cloudy on long standing.
2 per cent. S. C., 98 per cent. hem., very slight ppt., liquid cloudy on standing.
5 per cent. S. C., more ppt. liquid nearly clear on standing.
10 per cent. S. C., more ppt., liquid clearer on standing.
20 per cent. S. C., marked ppt., part up, part down, liquid quite clear on standing.

Digitized by Google

30 per cent. S. C., more ppt., otherwise same as last.
Up to 90 per cent. S. C. the volume of ppts. increased, but for the higher proportions a larger part of the ppt. settled to the bottom.

Chestnut (B) and S. C.
100 per cent. C., slight ppt., settling to the bottom.
2 per cent. S. C., slight ppt., indistinguishable in character from preceding but in larger amount.
5 per cent. S. C., similar to preceding, but more ppt., all to bottom.
10 per cent. S. C., ditto.
20 per cent. W. C., more ppt., half to top and half to bottom.
Up to 90 per cent. S. C., increasing quantities of ppt., much of which rose to the top.

Chestnut (C).
100 per cent. no ppt. visible at first. Slight ppt. on standing. Other results as with (B).

Valonia extract.
Straight, no ppt., but a slight cloudiness, persistent.
2 per cent. S. C., immediate ppt., liquid settles clear.
Up to 90 per cent. S. C. amounts of ppt. increase, all settling to bottom.
Other chestnuts examined behaved like the 2 mentioned. B. is liquid and C. powdered.

I tested Mr. Reed's suggestion in regard to the effect of the age of the aniline used. There seemed to be no difference among three samples, one fresh, one a year old, and one four years old, except possibly a somewhat heavier ppt. with the small proportions of S. C. for the oldest sample."

A series of experiments conducted in the laboratory with which the writer is connected seem to show that the Procter-Hirst reaction will give an unmistakeable test if sulphite-cellulose extract be present in a solution to the extent of 1 gram total solids to 2,000 c.c. of the solution, and this regardless of whether other material than sulphite-cellulose be present. In fact the delicacy of the test seems to be somewhat increased by the presence of a proportion of regular tanning extract. I purposely have used the total solids figure as the basis for the estimation of the delicacy of the test, as the reactive ingredient of S. C. extracts occurs essentially as largely in the so-called non-tans *i.e.* in the filtrate after treatment with hide powder as in the original extract solution. The exact limits of the test vary somewhat with different sulphite-cellulose extracts and with different mixtures. Below the above limit the deductions from the

Digitized by Google

test are uncertain, especially as there are some extracts free from added sulphite-cellulose material, which give a test with the Procter-Hirst reaction of about this order of magnitude. I might say that various samples of aniline, new and old, were used with these extracts and with no material effect on the results of the test. That extracts of this sort occur is of little commercial interest, as there would be no object in the use of so small amount of S. C. material for purposes of sophistication.

If we assume a limiting value such as the above for the delicacy of the Procter-Hirst test it is possible by a series of dilutions of a mixture containing suphite-cellulose extract to arrive at a very reasonably close approximation to the percentage present. The procedure is simply to make up a solution of the extract of usual analytical strength, then prepare a series of tubes containing this solution diluted with successively increasing amounts of water and note the dilution at which the test corresponds to that given by a solution of so-called limiting strength. Tests made by a member of the laboratory staff on unknowns, prepared by another member, gave results somewhat as follows:

Found	25	40	5
Present	20	50	5

This is perhaps rather better than could be generally expected.

Further work done during the past year on the Hayes reaction, as published in the report of last year's Committee seems to show that this test is not reliable. It obviously depends on the difference in solubility in acetic acid of the precipitates formed by gelatine and sulphite-cellulose and by gelatine and tannin, the former being less soluble. When the method was originated, an attempt was made to so proportion the amount of the reagents that in no case would any of the gelatin-tannin precipitate remain, but further experience seems to show that this was not accomplished. Several extracts, notably of quebracho and of chestnut, have been met which gave a strong test for sulphite-cellulose though none was present. The test doubtless has some value as a help, but cannot be regarded as dependable.

The writer hoped to be able to present data from several laboratories on the Levi-Orthmann reagent No. 33 and its usefulness in shedding light on the sulphite-cellulose question, but

Digitized by Google

regrets that he has only some rather limited data from the laboratory with which he is connected. Reagent No. 33 was prepared after the published directions with due care to secure pure materials and to follow directions accurately. Analyses were then made of various extracts by the hide powder method and with reagent No. 33. The results were not particularly promising, especially as suggesting that with this reagent we shall have a means of estimating quantitatively amounts of sulphite-cellulose in admixture with regular tanning extracts. Specimen results were as follows:

	Tannin	
	Hide powder	No. 33
Oak bark	24.7	19.2
Hemlock	26.5	18.4
Sulphited quebracho	39.2	36.0
Chestnut wood	31.3	16.9
Chestnut wood	29.0	16.3
Sulphite-cellulose (a)	21.2	9.8
Sulphite-cellulose (b)	16.7	9.0

As these results were secured with only one preparation of the reagent they cannot be regarded as weighing very heavily against the published results of the authors. Further data from a range of laboratories and on a variety of extracts must be secured before it will be possible to pass other judgment on the reagent than that it is a nuisance to prepare.

What work has been done by this year's Committee would seem to show that the Procter-Hirst reaction is reliable in so far as it always gives a test when sulphite-cellulose materials are present in amounts exceeding one part total solids to 2,000 of solution; that, however, there are certain extracts containing no added sulphite-cellulose which give a test but in which the percentage of sulphite-cellulose indicated by the test is so small as to have little or no commercial importance; further that the Procter-Hirst reaction can be used to show with fair accuracy the percentage of sulphite-cellulose material present in a mixture.

(After the reading of the report, L. Balderston described some preliminary experiments with Levi and Orthmann's "reagent No. 33." His results were not seriously different from those mentioned in the above report.)

Digitized by Google

NOTES ON DEPILATING.*

By Allen Rogers.

In presenting this paper for your consideration it has seemed wise to take up the subject under separate headings, thus giving, in a way, a short general review of some of the common processes employed in depilating. By so doing it will of course be necessary to discuss a great deal of ancient history, but it is felt that this is advisable in order to consider properly the more recent developments in this important step in the manufacture of leather.

Sweating. The oldest method of depilation seems to have been by means of incipient putrefaction, or as it is called "sweating." The hides were allowed to remain in piles in a warm, damp room until the mucous matter connecting the epidermis with the dermis had decomposed, which thus loosened the hair without injuring the true skin. This method, however, often resulted in damaged stock and so the process was improved upon by allowing the hides to hang in a closed, damp room or cellar called a "sweat pit." Two general methods are employed known as "cold sweat" and "warm sweat."

Cold Sweat. The cold sweat method is very largely used in this country, especially for unhairing dry hides for the manufacture of sole leather. The sweat pit is a structure which is usually built above ground and protected from outside atmospheric influences by means of a double wall between which and the inner wall is a filling of tan bark or other material to prevent loss of heat by radiation. The temperature of these pits is controlled by means of steam pipes running under the false flooring and a sprinkler system to provide moisture and to lower the temperature in case of necessity. The temperature is maintained at about 70° F. The hides are hung on hooks, each chamber holding a single pack. The sweating lasts usually four or five days. Near the end of the operation the stock is carefully examined and those hides showing the first signs of slipping are dropped to the floor in order to retard the putrefaction, it being cooler on the floor than higher in the pit. At the conclusion of the process the hides are thrown into lime liquors for

*Read at the *A. L. C. A.* Convention, Atlantic City, Dec. 5, 1913.

Digitized by Google

a short time in order to remove the slimy feel and to slightly plump the stock. The value of this process depends upon the fact that the hides are left in a firm condition without any appreciable loss of hide substance, but even if most carefully conducted there is great danger from excessive putrefaction, with a consequent damage to the grain. Although this process has its disadvantages, dangers, and shortcomings it is very widely used and no doubt will be continued for some time to come.

Warm Sweat. The warm sweat method is very similar to the cold sweat process, except that a higher temperature, about 80° F., is used and the time of treatment is somewhat shorter. It is applied more especially to sheepskins and is known as "staling." This process is not employed to any extent in this country.

Liming. The first chemical method of depilation was that in which slaked lime was employed. Although this material has been used for many years, the methods of application do not differ materially from those in vogue a century or more ago. Lime which is to be used for unhairing must be as free as possible from magnesia, clay or iron as these materials not only diminish the lime content, but cause the lime to slake much more difficultly and the iron, being insoluble, becomes fixed in the grain with the subsequent production of stains. It is hardly within the scope of the paper or the time at my disposal to go into the details of making up a lime liquor. In passing, however, I do want to bring attention to a statement which is often made, that, owing to the limited solubility of lime in water, (1.3 parts per 1,000 at 70° F.), there is no danger of destroying a pack of hides or skins by using an excessive amount. Personally I feel that this statement is misleading. There is probably no danger of destroying the stock, but there is great danger of damaging it by improper lime treatment. This is a point which I will take up again. That lime can be and is used in various ways is evidenced by the fact that if we should visit 100 tanners I would be willing to wager that we would not find two plants using the same method of liming. Yet lime is a compound which is only slightly soluble in water and according to theory its beneficial effects can only come from what goes into solution and providing that we always

Digitized by Google

have an excess present the results should always be the same no matter how much we may care to use. That this is a case where theory and practice do not coincide will be shown from experiments conducted with this end in view.

Many tanners claim that in order to unhair a hide properly it is absolutely necessary first to treat the stock with old lime liquors, gradually bringing the hides into fresh lime solutions. That there is some foundation for this belief will be shown, but there are limitations, which must be observed. There is no doubt that old limes do have a softening effect upon dry hides, due to the putrefactive action of the bacteria which they contain, for it has been shown that putrefactive bacteria are present in old limes. That they subsist upon the mucous matter between the epidermis and dermis as well as upon the connective material between the fibers has also been shown. But are we sure that they only care for the mucous matter and connective material? Are we not safe in assuming that if they will attack these materials they will also act upon the fibers or gelatinous matter as well? Do we want to run the risk of damaging or perhaps destroying valuable hides and skins by serving them as a rare morsel to a lot of hungry bugs whom we do not know and with whom we are not in sympathy? Would it not be better to depend upon the soaks for securing the soft condition we desire and not upon the uncertain action of putrid lime? In my humble opinion we should not depend upon a lime to soften a hide as this should be done in the soaking process. But as the soaking of hides is not to be considered we will not enter into the discussion.

It is claimed by some that it is impossible to unhair with fresh limes, but those who make such a statement have evidently never tried to do so. It is not my intention, however, to try to convert those who are using putrid limes, but rather to give some of the salient points which have developed as the results of a series of tests which have extended over the past two years and which were carried out at the suggestion of the National Association of Tanners. These investigations have already been printed in phamplet form and probably have been received by those present. The points which have been paramount in all of these investigations have been the determination of weight, measurement and

Digitized by Google

the condition of the leather obtained when the various well known and commonly used depilating agents were employed. In conducting the experiments it has been the endeavor to approach as closely as possible to the actual working conditions as they exist in the tannery and to observe not only the chemical action taking place, but to note the physical changes as well.

For the purpose, however, of corroborating the analytical data obtained during the practical tests, a series of parallel tests were made in the Laboratory on small samples of stock. The material used in these laboratory tests being shaved free from hair at the start so that this factor of uncertainty might be eliminated.

The first series of practical tests was for the purpose of determining the effect of various amounts of lime on the stock as well as the influence of the time of treatment. Both fresh and bettered limes were employed. Several packs of skins were treated with 5 per cent. of lime and at the end of two days showed an increase in weight of about 40 per cent. above the trimmed weight. The lime absorbed was about 1.30 per cent. Several packs were then run with 10 per cent. of lime and gave an increase from the trimmed to second day out of lime, of 50 per cent. with an absorption of 3.65 per cent. of calcium oxide. One lot treated with 10 per cent. of lime gave an increase of 61 per cent. with an absorption of 3.09 per cent. of calcium oxide. These results seem to indicate that the larger amount of lime produces a greater increase in weight and causes a greater absorption.

An experiment was made to see if one portion of lime would completely depilate a pack of hides. For this test 10 per cent. of lime was added to the stock in the paddle and without changing was allowed to remain in the same liquor for 10 days. At the end of this time the hair was only partially loosened, it requiring immersion in warm water and considerable work in beaming before the hair was completely removed. Thus we had an excess of lime always present, but for some reason the changes which had taken place greatly retarded the depilating effect. An interesting fact in connection with this pack was that after 8 days the lime in the solution increased again showing that it was being drawn from the hides.

Digitized by Google

In conducting the analytical work, the loss of hide substance was always observed. In all cases where the lime was applied fresh the loss was greater than when the lime was bettered. This would seem to indicate that new lime has a greater solvent action upon what we call hide substance than does an old lime. May it not be possible that in the old limes we have a protective colloid formed? To illustrate this point if a pack was treated with fresh lime run for a day, the lime discarded, a fresh lime made up and so on for a number of days, the loss of hide substance was much greater than where the stock had been bettered with the same amount of lime. In the pack cited above as being treated for 10 days it was very interesting to note that the amount of dissolved hide substance increased but slightly from that found after the second day. From the appearance of the resulting leather, however, there can be no doubt that some action had taken place which had a decided influence upon the character of the product. Attempts were made to determine the amount, if any, of volatile matter given off during liming, but no satisfactory results were obtained.

The record of pack weights at different stages of liming showed, without exception, that the greatest weight occurred on the fourth day. This was due to the fact that up to the fourth day the lime was being absorbed, but the action was not sufficiently great to cause the hair to drop off. The decrease following the fourth day was due to the loss of hair. This was shown pretty conclusively in the laboratory tests where the hair had been eliminated before treatment. These showed no loss after the fourth day. It may be of interest to note a typical increase from samples which were freed from hair and depilated with 5 per cent. of lime which was made fresh each day and from a series treated with 5 per cent. of lime bettered each day:

	Fresh	Bettered
Percentage increase after 1 day	42.10	42.93
Percentage increase after 2 days	2.60	2.10
Percentage increase after 3 days	4.14	4.10
Percentage increase after 4 days	1.30	1.41
Percentage increase after 5 days	1.70	1.70
Percentage increase after 6 days	0.30	3.60

These results are of interest as showing that about 80 per cent.

Digitized by Google

of the total increase in weight occurred during the first day. From this we might predict that the absorption of lime should give a similar condition. To show however, what did happen to hides treated with fresh and with bettered lime the following results may be noted.

	Fresh		Bettered	
	Ash	CaO in ash	Ash	CaO in ash
Original dry weight per cent..	0.66	33.67	0.51	32.80
After 1 day	3.15	59.82	3.14	56.61
After 2 days	3.30	74.45	3.71	78.98
After 3 days	4.25	76.58	4.19	80.49
After 4 days	4.52	78.46	4.50	90.64
After 5 days	4.21	86.69	4.81	86.07
After 6 days	5.18	82.69	4.67	84.23

The practical tests coincided with these laboratory experiments showing that most of the lime was taken up during the first two days. Both the practical tests and laboratory experiments show that the absorption of lime is not wholly responsible for the increase of weight. In other words the absorption of lime and the absorption of water do not bear any definite relation to each other. The higher ash in the fresh lime treated stock would seem to indicate that the fresh lime has a greater solvent action on hide substance than does the bettered lime treatment. This is shown by the fact that the ash is higher in the former case, while the lime in the ash is less. This would again indicate that possibly used lime may have a protective colloid effect.

It is generally assumed that during the liming process fat in the hide is saponified, thereby producing a lime soap and that the formation of this soap tends to open the fibers. That this saponification is not complete is shown by the following results:

	Fat on dry weight	
	Fresh lime	Bettered lime
Fat, original per cent.....	5.11	5.21
Fat after 1 day	1.86	2.77
Fat after 2 days	2.05	1.96
Fat after 3 days	1.24	1.96
Fat after 4 days	3.01	4.43
Fat after 5 days	1.22	1.05
Fat after 6 days	1.25	2.88

Although these results are not very concordant they do show

Digitized by Google

that practically all of the fat which was saponified becomes so in the first 24 hours. This would perhaps account for the increase in weight of the stock during the same period. It seems fairly safe to say that 75 per cent. of the fat was saponified during the first day and after that practically no more saponification took place. This is very closely related to increase in weight when we remember that practically 80 per cent. of the increase in weight took place during the first day.

Many tests were run in the laboratory as well as on a practical scale to determine the loss of hide substance occurring in the lime liquors. The following examples will illustrate what has been observed:

	Fresh lime	Bettered lime
Per cent. of hide substance lost after 1 day	0.51	0.55
Per cent. of hide substance lost after 2 days ...	0.253	0.39
Per cent. of hide substance lost after 3 days ...	0.43	0.59
Per cent. of hide substance lost after 4 days ...	0.66	0.64
Per cent. of hide substance lost after 5 days ...	0.24	0.17
Per cent. of hide substance lost after 6 days ...	0.25	0.34

These data are of interest from the fact that if we add the first column we will have a loss of hide substance amounting to 2.143 per cent. The second column if added would give about the same result, but as a matter of fact the second series of tests are for solutions which had not been changed and indicate the amount of hide substance which had dissolved during the time the stock was in the solution. In the first series the solution was made up fresh each day. In the second series the same solution was used continuously, new lime being added to the old solution. These results need some explanation. Do they show us again that after a lime has been used for one day that some change has taken place which protects the so called hide substance? It may be possible that the hide substance which has been dissolved changes rapidly into some form which does not respond to the tests applied for hide substance. Similar results have been noticed on the practical tests, although in these instances a somewhat larger amount of hide substance was observed. The question now comes up: What do we understand by hide substance? It is pretty well agreed that hide substance does not necessarily mean gelatin, but rather the albuminous material present as con-

Digitized by Google

nective tissue between the fibers and the layer between the epidermis and true skin.

From the observations noted above it seemed fairly safe to assume that the proper manner to apply a straight lime solution would be to enter the stock into a lime liquor which is only a few days old at most and then to work up through the series to a fresh lime liquor. The lime which has been used thus for the new pack should then be discarded. This does not mean, of course, that we can lay down a hard and fast rule which will work for all classes of stock, but is to be interpreted as being in the nature of a general procedure. It may be mentioned at this point that "Hydrated Lime" is rapidly replacing slaked lump lime for tannery use and has many advantages over the older form.

Sodium Sulphide. This material is very largely employed as a depilating agent. It may be used alone or in conjunction with other substances if desired. When used alone it has the property of rapidly and completely dissolving the hair, but causes the stock to plump excessively, with the production of a false grain and loss of measurement. It has its advantages as a time saver, produces more weight and a tight grain. The usual method of using a straight sulphide solution consists in making up a 20° barkometer liquor at a temperature of about 75° F. The stock is then placed in this liquor, run for two hours, allowed to rest over night, run for half an hour, washed, neutralized with sodium bicarbonate and then again thoroughly washed.

For some classes of leather the sulphide is made into a paste or a very heavy liquor and applied to the flesh side. Skins so treated are piled down over night and on the following day the hair may be readily removed by hand. This method is the one commonly employed by wool pullers and by tanners of other grades of stock carrying valuable hair.

Sodium sulphide mixed with lime very materially helps in the removal of fine hairs. For this purpose about 20 per cent. of sulphide upon the weight of the lime is sufficient. The sulphide should be added to the lime before slaking. For hydrated lime and sulphide mixture the two should be boiled together. Whenever sodium sulphide is used in conjunction with lime it

Digitized by Google

should be at the start of the unhairing process. Many tanners, however, use the sulphide after the stock has been limed for several days. This would seem to be very poor policy if its addition is for the purpose of removing fine hairs. The reason for this statement is based upon the fact that sodium sulphide has no solvent action upon hair which has once been treated with lime, no matter how strong the sulphide solution may be made. On the other hand clean hair will rapidly dissolve even in dilute solutions of sodium sulphide. A very good system and one which has been found to give satisfactory results is to use a series of three or four pits adding the sulphide required to the oldest liquor when the new stock enters, the head pit being straight lime liquor. No loss of hair occurs by this treatment although the stock is free from fine hair and has the appearance of limed stock, except that it has a better grain than is obtained with either sulphide or a long lime treatment. To determine the effect of this lime and sulphide mixture several practical tests were made with a five to one combination. The grain in weight from the soaked to the first day out of the liquor was 43.24 per cent., during the second day the gain was 2.45 per cent., while after the third day, there was a loss of 0.55 per cent. The loss was caused by the complete slipping of the hair. The amount of lime absorbed increased from day to day, but no more sulphide was taken up after the second day. The laboratory tests conducted along the same line did not agree very closely with the practical tests, owing to the previous removal of the hair. The analyses of the hide samples, however, gave some results which may show that there is a reason why lime stock is not so tight grained as stock treated with sulphide. For example we might note the following:

	New	1 day	2 days	3 days
Per cent. of fat.....	3.55	1.19	1.57	2.11
Per cent. of ash	0.67	2.35	2.71	3.07
Per cent. CaO in ash..	31.60	68.20	69.10	75.92

There records show that the per cent. of fat remaining after the treatment was about the same as noticed for lime stock. The absorption of lime was somewhat more after the first day than was observed for straight lime treatment, but on the third day it had increased to that of limed stock. We can pretty safely

Digitized by Google

assume that the lime would continue to be absorbed if a longer treatment had been given.

In the practical tests with straight sulphide solution the gain in weight after one day was considerably less than with any of the previous treatments, being about 16.25 per cent. This was due of course to the solvent action of the sulphide upon the hair. One pack was treated for four days with the sulphide, but showed very little gain after the first day. The hair free laboratory samples, however, showed a gain of more than 50 per cent. after the first day. Analyses of the hide gave the following:

	New	After 1 day
Per cent. of fat	6.70	1.90
Per cent. of ash	0.44	0.94

One might expect the stronger alkali to more completely saponify the fat, but the data obtained do not seem to bear this out. Analyses of the liquor showed that the stock, at the end of 24 hours, had absorbed 0.126 per cent. of sodium sulphide and 0.124 per cent. of sodium hydroxide.

Among several other methods of depilating which were studied should be mentioned one in which a mixture of sodium sulphide and calcium chloride were used. The advantages of the method were found to be in the freedom from false grain, complete removal of hair, saving of time and better measurement than straight sulphide. The method consisted in running the stock in a 20° barkometer sulphide solution to which had been added one fourth as much calcium chloride as there was sulphide used.

Arsenic Sulphide. This material was used in several tests and owes its value in depilating to the fact that it produces a sulphide of calcium without the introduction of the caustic alkali which is formed when sodium sulphide is used. This material is used very extensively by the goat skin and glove leather manufacturers where an open leather with a smooth grain is desired.

Tryptase. During the past year a new unhairing agent has been brought to the attention of the trade. This material it is claimed will unhair and bate in one operation. If this new product comes up to its claims it will certainly be a God-send to the tanner.

Digitized by Google

In closing this feeble attempt to say something about depilating let me emphasize the point that after making a fairly careful study of the subject for the past two years, and having been in pretty close touch with beam house methods for the past 15 years, I have come to the conclusion that we know very little indeed about the subject from either a practical or a scientific standpoint. It is a field, however, which offers wonderful possibilities for research work and I for one sincerely hope that it will receive more attention in the future than it has in the past.

THE INTERPRETATION OF TANNERY ANALYSES.*

By W. H. Teas.

Without a reasonably accurate interpretation of tannery analyses much of the value of the analyses is lost. Lack of this interpretation and much inaccurate interpretation has retarded the adoption of laboratory control of the tannery. Since we are dealing with organic materials in the vegetable tanning industry, we cannot hope to evolve a list of hard and fast causes and effects, as it has been possible to do in the case of the manufacture of inorganic materials such as steel. There are so many conditions that affect the operation of a tannery, that there are only a few cause and effect combinations that are general. Those who have had the opportunity of watching from week to week, the results of systematic analyses from a number of tanneries, while at the same time watching the development of the leather in the tannery, know the truth of the foregoing statement.

The raw materials used, the purity of the liquor, the acidity, the relation of the tannin figure to the acid figure, the ash, etc., are items that have been developed and recognized as bases of comparison. And too frequently, interpretation and diagnosis are made on these bases without any regard to the many other conditions that are important factors at each particular tannery. It is quite true that there will be many glaring deviations from normal figures for the above items, which will at once point out the trouble. But it is also true that many tanneries showing

* Read at the *A. L. C. A.* Convention, Atlantic City, Dec. 6, 1913.

Digitized by Google

normal data in the analysis figures are not doing good work, and one must look beyond the usual laboratory determinations for the answer.

The character of the water used, the soaking procedure, the methods of the beam-house, the methods of handling the yard liquors and of the leather in the yard, the bleaching, scrub-house operations, oiling, lofting, and finishing, are, all of them, important factors whose influence and variations are not shown by analyses of samples usually sent to the laboratory. Quite frequently, causes are assigned based on liquor analyses, for effects for which the liquor is not responsible.

Insufficient soaking is sometimes responsible for hardness and bony streaks in the leather, that may be blamed on the liquors. Too much lime, or the failure to remove as much lime as possible before going to the rockers, frequently produce results for which the liquors are blamed. And so on through the list of trouble opportunities which are always present in the tannery, and which cannot always be located by laboratory examination of samples.

Even when given accurate description, or even samples of the product, the chemist is confronted with many conditions which may be produced by more than one cause. Thin grained leather, for example, might be caused by liquor conditions or by beam-house work; flat thin leather might be caused by one of several liquor conditions widely different. There is more than one tannery condition producing cracky tender leather. And so I might instance many other troubles having as possible causes, more than one condition of liquor or procedure. Methods of handling tannery liquors, and of the sequence of their application to the hide, are of course factors in producing certain results; and the same methods are successful at one tannery and failures at another. The apparently unimportant item of the amount of leather put in a layaway vat, is very frequently a trouble factor, and has a direct influence on the action and character of the liquor.

The purpose of this monograph of commonplaces, is simply to sound a warning note to the tannery chemist, on the subject of diagnosis and interpretation. None of us has had too much tannery experience, and most of us have had too little. A year

Digitized by Google

in the tannery is worth three in the laboratory, so far as developing a faculty for interpreting laboratory results is concerned. And if a tanner maintaining a laboratory would arrange so that the chemist could spend a certain time in the tannery daily, the value of the laboratory to the tanner would increase, and the increase would be measured by the capability and practicality of the chemist.

The most experienced water analysts will not pronounce judgment on a drinking water from a sample of the water, and they insist in having all possible data as to conditions which may influence the purity of the supply. The tannery chemist should be similarly conservative in his interpretations based on samples alone. The cause of the tannery chemist has been hurt more by faulty judgment and recommendations, than by poor analytical work. A plain "I don't know," is in most cases a safer answer, than a guess with insufficient data to make a different answer more than a guess. Better have the tanner think the chemist doesn't know much, than to have him foot the damage bill because the chemist thought he knew, and didn't know. In the one case, the tanner will probably come back, but in the other case he will not return. And you will find that the latter experience will get more publicity than confessed inability to answer.

I don't mean these remarks to apply to those glaring abnormalities previously mentioned, and which experience has shown are conclusive in their meaning. To the chemist with any tannery experience at all, that kind of problem is easy and its soultion certain. But under conditions of contradictory symptoms, accompanied by lack of data, by all means be conservative. If the trouble warrants it, get on the ground; and even then, don't make a recommendation that will entail loss by its failure, unless you are certain that you have a successful remedy.

The chemist in the tannery has come to stay; the numerical growth during the past ten years, the institution of the tanning school, and this Association itself, are all proofs that we are to be permanent. We might claim that we are no longer luxuries, but almost necessities. We are like the church, in at least one

Digitized by Google

respect, in that we as a class are judged by the mistakes of our members. Conservatism will certainly lessen our mistakes, and if accompanied by the opportunity of practical work, it will not materially retard the universal recognition of the necessity of the chemist in the tannery.

INDUSTRIAL CHEMISTRY AND THE LEATHER INDUSTRY.*

By Charles R. Oberfell.

We are accustomed to read in current literature frequent and sometimes detailed reference to the mechanical progress of this age and many can remember the introduction of the telephone and telegraph, while the perfection of electrial machinery, the advent of the aeroplane, automobile and wireless telegraph have crowded upon us in such rapid succession that we cease to wonder at new marvels. At the same time the progress in chemistry, which so vitally effects civilization, and especially its application to the industries has failed to win the merit of public acclaim to which it is justly entitled, on account of the popular mind seizing with more comprehensive understanding the mechanical marvels.

Perhaps to this gathering of chemists and tanners a rapid survey of the most important industrial developments brought about in manufacturing processes by the touch of the chemist will not be uninteresting, and may bring us to a keener realization of the fact that on us and our fellow workers abroad devolves the responsibility of placing the leather industry, which is essentially a chemical process, on a firm scientific basis.

It is impossible to select from the recent advances in the application of chemistry to the industries the most important or a group of most important ones. One of the most interesting, and one which brings us into touch with the leather industry has been the commercial development by Dr. L. H. Baekeland of the class of compounds, known as the condensation products of formaldehyde and phenol, and sold under the trade name Bakelite. Dr. Baekeland's researches are classical and stand as an exponent of the possible under the guidance of a wonderfully scientific

* Read at the *A. L. C. A.* Convention, Atlantic City, Dec. 6, 1913.

Digitized by Google

mind. Lately Stiasny has utilized much the same class of reactions in the production of a synthetic tannin called neradol, which is a condensation product of a sulfonated phenol with formaldehyde. Much has been claimed for this new tan-stuff and its advent may introduce a new era in the production of leather.

The tremendous use of the natural supply of nitrates as fertilizers has brought with it a realization of the fact that the ultimate exhaustion of such deposits is but a matter of a relatively few years. Fortunately and at this opportune time we find the chemist's work allaying all possibility of a famine in nitrates by the development of processes for the utilization of the nitrogen of the air. The processes whereby nitrogen is brought within the reactive sphere are of three types. Firstly, direct oxidation, or the union of oxygen and nitrogen in the electric arc. This process was made possible by a development of stupendous electric power as typified in the plants at Niagara Falls and in Norway. In Norway it is estimated that the electric furnace and electro-chemistry will in a few years double the population of that northern country and give employment to thousands upon thousands. Secondly, the fixation of nitrogen to the metals and metalloids, the most prominent product being calcium cyanamide by the union of calcium carbide and nitrogen. The nitrogen of this compound is available as plant food or may be freed as ammonia by the action of steam. Thirdly, the direct union of nitrogen and hydrogen, in the manufacture of synthetic ammonia, in the presence of catalytic agents and under favorable temperature and pressure conditions. The researches of Haber, painstaking and extending over a long period, resulted in the first successful plant.

Kirchhoff's discovery of the inversion of starch to glucose with dilute acids has profited the United States alone by over $30,000,000 a year and made possible the corn products industry which yields such products as glutten, starch, glucose, dextrin and oil.

Another development brings us close to the leather industry again in the hydrogenating or hardening of oils with the formation of solid greases. By the addition of hydrogen, in the presence of suitable catalytic agents, to oleic acid we have stearic

Digitized by Google

acid. This reaction is merely typical of a class, and these hardened oils are finding wide use in the currying of leather besides their use in soap manufacture and as edible products.

The ammonia soda process developed from the discovery that sodium bicarbonate is insoluble in ammoniacal brine has revolutionized the alkali industry and cheapened a product of universal consumption. Again industrial chemistry touches the leather industry.

The simultaneous discovery by Hall in this country and by Héroult in France that aluminum is obtained by electrolizing a fused mass of cryolite and aluminum-bearing clays was the beginning of a wonderful industry and brought about a reduction in the price of aluminum to 23 cents. Plants operating under Hall's patents are located at Niagara Falls; and here too, due to the electric energy available, are made carborundum, a valuable abrasive, and artificial graphite, the last two as the result of Acheson's researches.

This year Gayley was awarded the Perkin medal for his researches which resulted in the perfection of the dry-air blast used in the manufacture of steel, and it is estimated that the work of this chemist in this one particular alone makes a saving of at least $20,000,000 a year. Gayley employs refrigeration for the elimination of water from the air before it is driven into the furnaces.

The use of the newer forms of electric lamps, involving a great saving to consumers, was made possible by the researches of Whitney, a past president of of the American Chemical Society, and his staff of chemists in the wonderfully equipped research laboratories of the General Electric Company.

The reclamation of valuable products from wastes in the wool industry, such as oleic acid, distilled oleins, soaps, lubricating oils and refined wool greases brings us to the application of these products in leather currying and the fat-liquoring of chrome tanned leather.

Wonderful has been the development, with which you are all familiar, in the coal-tar industry. It is impossible to estimate the amount of capital invested as the result of Perkin's discovery of mauve.

Digitized by Google

Chemistry has given the world virtually two new fabrics in artificial silk and mercerized cotton.

Time will not permit a further discussion of these many wonders, but I shall merely mention a few of the more important triumphs of chemistry. The Bessemer process for steel—Powerful explosives, the like of which the world has never known—Contact sulfuric acid and great improvements in the older chamber process—Improvements in the manufacture of paper and pulp—The Welsbach gas mantle—Liquefied gas in the Blaugas system—Steel alloys of chromium, vanadium, manganese, tungsten and molybdenun—Desulfurizing petroleum, and the claiming of untold quantities of sulfur 1,000 feet below the surface in Louisiana; the last two achievemants by Frasch, another recipient of the Perkin medal.

These achievements which have added untold wealth to the world, have not been the result of chance or haphazard investigation, but are the product of brains and chemistry, working hand in hand with engineering skill, and not of least import, the co-operation of capital. In order to bring about the discovery of the great fundamental reactions underlying the processes enumerated and their expansion from laboratory size into great commercial enterprises it has required years of study and research in completely equipped research laboratories. Scientists are generally familiar with the extent to which research has developed in Germany and in fact all over Europe. In this country it is still in its infancy. In Germany the large chemical manufacturing plants maintain an unexcelled equipment and a large staff of chemists, whose sole occupation is not control of the processes of manufacture but a continual search for new processes and products.

The need which the leather industry, in its many phases, faces, and which has been made acute by the scarcity and high cost of raw materials is greater efficiency, and this can only become possible, in its highest development, through organized research effort. As we all know the processes of leather conversion are fundamentally chemical in nature, yet after all these years the production takes place along empirical lines, and we as leather chemists do not fully understand the exact nature of the

Digitized by Google

materials we deal with nor the principles of the conversion of hide tissue into leather with all of its many ramifications.

The A. L. C. A. and I. A. L. T. C. have made great strides and there is no questioning the high plane on which the two associations have placed the analysis of tanning materials. It is doubtful if a similar triumph can be pointed to in any branch of chemistry in view of the difficulties, yet what the leather industry needs to place it on a plane with the other chemical industries is organized research. Our many manufacturers of leather who have equipped experimental and control laboratories of their own have made a great stride towards providing for the time, which will come, when the present empirical manner of production will prove so wasteful as to narrow the margin of profit to such a point as to force the small producer out of business, unless he has taken advantage of what chemistry offers. I venture to say that the day will come when leather will be produced by large business organizations and when every plant will be conducted on strict scientific lines and will have its laboratory and be as dependent on it as the steel plant is dependent on the steel chemist to-day. This will be the natural result of economic conditions and I do not fear that research will not steadily open up the avenues of advancement.

What is needed to-day is a more profound search for a solution of our present baffling problems, and a closer co-operation between producer and chemist so that the chemist may be encouraged to forge ahead into new fields and that the producer may better understand what he is dealing with and learn how to interpret the results of the chemist.

Research laboratories for the solution of problems in the leather industry will not be wanting for material on which to work, for besides the rich field of investigation on raw materials every step from the curing and disinfection of hides and skins to the finished product through the various manipulations necessary is full of imperfectly understood reactions. What of the reactions involved in the removal of the hair and their resultant effect on the quality and quantity of leather? What of the unknown composition of the tanning liquors? Volumes already have been written on acids in tan liquors and yet all of these

Digitized by Google

acids have not been isolated and measured nor their effect in combination with hide on the various tanning agents determined. Procter has pointed to this in recent writings. There are other non-acid substances in tan liquors that have never been studied, and we must also know the effect of the mineral constituents at the same time, which include the question of water used. There are losses in tanning and extracting tannin from raw material, but the extent of these losses and leaks are not known, nor where nor why they occur.

These are but a few of the unsolved problems, but they are enough to stimulate careful thought and planning for the future. Our present plant laboratories can not alone delve through this whole mass in the required time, for the successful study of such problems should be pursued uninterrupted with routine control and contract work. Also to pursue these problems successfully there must be a connection between research and practice. One of the greatest hindrances to the present properly trained and experienced leather chemist is lack of equipment for trying ideas originating in the laboratory. The peculiarities existing in leather manufacture, notably the consumption of time and the probability of easy and severe loss, preculde the advisibility of experimenting on a manufacturing scale. What is required is opportunity, that is, equipment and funds, so that the ideal condidtion of practice and theory may be possible. Some of our largest industries to-day maintain small fully equipped plants for such study.

The proposed Procter International Research Laboratory is the first step in the right direction and Prof. Procter, its director, is without an equal for such study as will be pursued there. This project deserves the support of all interested in the leather industry, for the result of its researches will be for the benefit of all and should receive the support of all who will profit by it, both chemists and tanners.

In concluding I can but point to the great chemical achievements of this age, which came as the result of organized industrial research, to show that the same kind of effort for the hidden truths must take place in the leather industry to place it on the same high plane.

Digitized by Google

Discussion.

In answer to a question, Mr. Beye said that it is the intention of those charged with the direction of the Tanners' Institute in Brooklyn to develop there a real research laboratory. Such a laboratory will require time for its development, and the co-operation of the A. L. C. A. Mr. Veitch said that the Bureau of Chemistry has good intentions in regard to carrying on research work in connection with leather problems. The present head of the Bureau is favorably disposed, and the prospect of something being done is brighter than ever before. This prospective activity on the part of the Government Bureau should not, however, hinder the establishment of other research centers.

BOOK NOTICE.

Leather Trades Technical Dictionary. Ferdinand Kohl. "Ledermarkt" Press, Frankfurt a. M., Germany. This book contains about 7,650 German technical terms connected with leather, with their equivalents in English and French, arranged in parallel columns. To be more precise, the terms include any which are likely to occur in technical or scientific articles in regard to leather. Thus such words as refrigeration, lighting, salary, fresh, foot, and a multitude of others that are here which are not exactly special leather terms. The value of such a book to any one who has to read articles in German and French leather journals is very evident.

The author in his preface acknowledges his indebtedness to his father, the late Emil Kohl, and to Mr. R. W. R. Mosely of Birmingham and also to Mons. M. Imbert of St. Pardoux la Riviere.

The number of mispelled words in the English column is negligibly small, and a pretty careful examination indicates that the leather vocabulary is remarkably complete. The price is 4.00 marks, postpaid.

ABSTRACTS.

Classification of Hides. *Leather Trades' Review*, November 5, 1913. A discussion of the differences between the tanners on the one hand and

Digitized by Google

the butchers and hide merchants on the other which have culminated in a combination of tanners to force hide inspection and classification.

Neutral Inspection of Hides. *Shoe and Leather Weekly.* The National Association of Tanners has sent out the following circular to the members of their association, under date of November 10:

Communication has been received from a newly-organized association, entitled "The Hide, Leather and Allied Trades Improvement Society," which is, we understand, an organization established by members of the United Tanners' Federations of Great Britain and Ireland, for the distinct purpose of establishing a new and improved method for the purchase of hides and skins.

The plan contemplates that there shall be a neutral inspector to be paid share and share alike by the seller and purchaser of hides at the rate of one cent each per each hide inspected.

It shall be the duty of this inspector to imprint upon each inspected hide on the flesh side at the tail an official stamp, which shall be a warranty of weight and selection. Hides not bearing this official stamp may safely be considered as of inferior quality and unwarranted weight.

This new order of things, to be adopted by no less than 80 per cent. of the tanning interests of Great Britain and Ireland, is to become operative commencing December 15 of this year. It is pointed out that commencing with that date, unless tanners in other parts of the world are properly advised and govern themselves accordingly, they will be offered hides (not officially stamped) which in all probability will be inferior in quality and unwarranted in weight, and that foreign buyers purchasing hides from Great Britain and Ireland which do not bear this official stamp not only will suffer in the first instance, but will work against the worthy efforts of the English tanners to establish a very fair and meritorious betterment in hide marketing conditions.

American tanners, therefore, who purchase in the English markets are earnestly requested to instruct their buyers, commencing with December 15, to purchase only those hides which have the official mark of a neutral inspector. There may be a temporary disadvantage to the individual tanner in so doing, but to the far-sighted man (and he does not have to be very far-sighted) no further suggestion is necessary.

It was ordered at the annual meeting of the association that this matter be brought up before the members and that a free written discussion be invited in answer to a circular to be sent out by the association. You are, therefore, invited to address our hide committee, giving your views on the above matter not only with respect to its application to Great Britain and Ireland, but with respect to a possible application of the principle in our own markets.

Very truly yours,
THE NATIONAL ASSOCIATION OF TANNERS.
212 W. Washington St., Chicago, Ill.

Digitized by Google

The Conservation of Hides. A. H. LOCKWOOD. *Shoe and Leather Weekly.* The author points out the difficulties in the way of legislation forbidding slaughter of calves. Dairying is a separate business from cattle raising, and it appears impracticable to add beef raising to the dairying industry. The dairy calf is not suitable to be raised and fattened for beef, as a rule. Any attempt to pass such a law would be certain to be vigorously opposed by the dairy industry. No laws prohibiting the killing of calves are likely to become effective in the immediate future. The author hopes that the raising of beef cattle by cereal farmers will become more general. The use of worn-out eastern farms for grazing grounds is suggested This would restore the fertility of the soil, and might in the long run become a paying proposition. The author hopes that the possibilities of Mexico and parts of South America as cattle raising countries will soon be more fully developed, and that the projected beef ranches of South Africa will be a fruitful source of supply within a few years. In many parts of the world the goat takes the place which cattle occupy in this country and Europe as sources of food and profit, so that the extension of cattle raising into these regions is not to be expected. In the conservation of the hide itself, the great rise in price has resulted in great reforms. The number of hides now imported into the U. S. in the dry condition is much less than formerly. The next reform should be in the direction of better take-off and cure. With the gradual passing of the ranges, brands are disappearing, but wire scratches and other such injuries may be further guarded against. The prevention of salt-stains and injury from tags are matters of importance. The Texas tick has been almost eradicated, but the grub is still here. Cattle men say that the researches made in Europe in regard to the warble are valueless here because the life-history of the American pest is different. Pressure should be brought to bear on the Department of Agriculture to make investigations to determine whether the observations made in Europe are applicable in America.

Hydrated Lime. H. E. BACHTENKIRCHER. *Chemical Engineer*, Nov. 1913, pp. 189-93. The process of manufacture is described briefly. (See this J. 1912, pp. 165-70.) Hydrated lime is not satisfactory for the making of mortar, since its colloid character has been lost in drying, so that it does not make a tenacious paste. Efforts toward solving this difficulty are meeting with some promise of success. Microscopic examination shows the hydrated lime to be in a crystalline condition. Lime slaked with insufficient water, called by masons "burnt" lime, is crystalline and will not make a smooth paste. Hydrated lime, because it can be kept conveniently and safely and because it can be transported in packages of convenient size, is finding wide use for all the purposes except mortar to which lime is applied. Among these are water softening, "waterproofing" cement, agricultural purposes, sweetening butter, and cleaning "smut" from grain. The author does not mention its use by tanners,

Digitized by Google

which appears to be increasing; (see Dr. Rogers' paper on depilation in this number.)

British Section, I. A. L. T. C. *L. T. Review*, Dec. 3, 1912, pp. 901-2. A meeting was held at Nottingham on Nov. 28th., jointly with the Nottingham Section of the Society of Chemical Industry. S. R. Trotman read a paper on Strychnine Tannate. J. T. Wood presented "Further Notes on Enzyms." Another session of the Section was held the following day, at which Dr. Stiasny presented the paper on Analysis of Vegetable Tannins which appears in the present number of this Journal. D. J. Law exhibited and described a specimen of basic calcium thiocarbonate. Dr. Turnbull reported that several samples of hide powder, although conforming to the official regulations, gave different results when used for the analysis of the same extract. The difference is owing mainly to he greater absorption of non-tans by one than by another. Dr. T. wanted the opinion of the members on the proposal that Paessler's powder should be adopted as the standard on condition that another powder should be used if it was found that Paessler's was deteriorating. He suggested that samples of certain extracts should be kept as standards for testing samples of hide powder. Dr. Stiasny gave the opinion that if two hide powders gave no soluble matter on washing, and if the non-tans showed no reaction for tannin, the powder giving the higher non-tans should be regarded as correct. A delicate test for tannin in the filtrate is as follows: To 3 cc. of the solution add 1 cc. saturated solution of NaCl, 2 drops 1 per cent. metaphosphoric acid and 2 drops of a solution containing 5 per cent. gelatin and 5 per cent. salt. No action was taken toward changing the rules. S. R. Trotman read a paper on "A Chromogenic Organism Decomposing Tannic Acid." From some skivers damaged by a pink discoloration, he had isolated an organism which, grown in a medium containing tannic acid, decomposes the latter, producing a brown stain. Growing in a medium containing no tannin, the organism develops no color. Grown in a tannin solution, it destroyed from 30 to 40 per cent. of the tannin in a week. Mr. Carter spoke of the variation in results in the analysis of extracts due to small variations in the temperature of filtration. E. C. M. Payne said that however careful the filtration, the results are fallacious, as much of the material reported as insoluble, is absorbed by hide and assists in making leather. W. J. Rivington reported that 90 per cent. of the money necessary for the building and equipment of the Procter International Research Laboratory has been contributed.

Retirement of W. Eitner. In the issue of *Der Gerber* for Dec. 15, 1913, Wilhelm Eitner announces that in consequence of advancing age and impaired health he is retiring from the editorship, a post which he has held since *Der Gerber* began, about 40 years ago. The JOURNAL voices the wish of all leather men that Mr. Eitner's health may be restored, and that he may long continue to write for the columns of *Der Gerber*.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. IX FEBRUARY, 1914 No. 2

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1914, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VEITCH, } . . . Past Presidents

OFFICERS, 1913-'14

PRESIDENT—W. K. ALSOP, Ridgway, Pa.
VICE-PRESIDENT—C. W. NORRIS, 80 South Street, New York, N. Y.
SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.
COUNCIL—A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y
LLOYD BALDERSTON, Ridgway, Pa.
C. R. OBERFELL, Harrisonburg, Va.
T. A. FAUST, 323 Academy Street, Newark, N. J.

ELECTIONS.

ACTIVE.

Samuel A. Neidich, Burlington, N. J.

ASSOCIATE.

Alfred C. Wessman, 531 W. 37th St., New York, N. Y.

CHANGES OF ADDRESS.

Henry W. Goodwin, to c/o Charles Case and Son, Leigh Works, Westbury, Wilts, England.

M. E. Mason, to 268 Fox St., Aurora, Ill.

J. C. Cover, to Elkton, Va.

V. Y. Shewade, to 825 Adams St., Gary, Indiana.

Harry M. Johnquest, to 1101 Broad St., Newark, N. J.

Digitized by Google

George W. Priest, to c/o Beaver Leather Mfg. Co., 28 Ferdon St., Newark, N. J.

Frederick L. Hilbert, to 50 River St., Winchendon, Mass.

C. H. Propach to 2340 Commonwealth Ave., Chicago, Ill.

Max. Meltsner, to 1329 Clay Ave., New York, N. Y.

COUNCIL MEETING.

At a meeting of the Council held at the Chemists' Club, New York, January 3rd, there were present Messrs. Alsop, Reed, Faust, Oberfell, Balderston and Norris.

The Editor was authorized to donate to the Library of Congress volumes 1 to 3 of the JOURNAL in accordance with the request of the Librarian.

It was voted to hold the next Annual Meeting in Chicago at the time of the meeting of the National Association of Tanners, during the last week in October.

The Secretary reported that subscriptions to the Procter Research Laboratory Fund amounted to a little over $600. It was determined to close the fund, and the Secretary was directed to write to the Secretary of the National Association of Tanners and ascertain if their subscription is to accompany that of our Association. The Secretary, when sending the fund, is to state that it is made up of individual subscriptions from members of the Association.

The Council approved the recommendations embodied in the report of the Committee on Sampling, approving Proposal A in reference to the quantity of solid, powdered and pasty extract to be sampled, and the proposed method will be submitted to a vote in accordance with By-Law No. 22.

COMMITTEES.

Sulphite-Cellulose Extracts.—It was decided not to appoint a committee this year, but Mr. Balderston was asked to submit to the Secretary in such form as to be voted upon by the Association a method for the detection of these extracts based upon the recommendations contained in the report of last year's committee.

Methods for Stating Results of Analyses.—Mr. Alsop was appointed chairman of a committee to endeavor to bring about a uniform method of reporting analyses; analyses of leather and

Digitized by Google

extracts were referred to especially. It was also suggested that it might be useful to have an official correction table for barkometer readings at different temperatures, and this was referred to this committee.

Fats and Oils.—Mr. Oberfell was requested to submit to the Secretary his recommendations as to methods of analyses for sulphonated oils, in order to submit them to a vote of the Association. He was appointed chairman of a committee to continue work on methods for these oils. Mr. Faust was appointed chairman of a committee to suggest methods for testing moellons, hard greases and hydrogenated oils.

Color Valuation of Tanning Materials.—Mr. Reed, chairman.

Determination and Estimation of Tanning Materials in Admixture.—Mr. Small was appointed chairman, and it was suggested that the committee test out methods with special reference to Mr. Kerr's method for the detection of mangrove.

Methods Dealing with Analysis in Connection with Beam House Procedure.—Dr. Allen Rogers, chairman.

Lactic Acid—Materials Used in the Manufacture of Chrome Leather—Miscellaneous Methods.—These subjects were grouped into one committee and Mr. Balderston was appointed chairman. Under "Miscellaneous Methods" it was suggested that the work of the committee should be a compilation of various methods.

Disposal of Tannery Waste.—Mr. Veitch, chairman.

Extraction—Suggested Use of Alundum Thimble.—Mr. Seltzer, chairman.

Acidity of Hide Powder.—Mr. Reed was delegated to send to numerous members of the Association samples of hide powder for determination of acidity and comparison of results.

Bureau of Arbitration on Tanning Materials.—Committee continued, with Mr. Haley, chairman.

S. & S. 590 Filter Paper.—This matter was left with the Secretary for attention in accordance with the suggestion made at the Annual Meeting.

The matter of testing for insolubles in solutions of extracts and liquors considerably stronger than those used for the Official Method of Analysis was discussed, and it was suggested that

Digitized by Google

individual work be done and the results published as a basis for future committee work if it should seem advisable.

The question was raised as to whether it was proper to analyze spent materials such as valonia, sumac and myrobalans according to paragraph 5-A of the Official Method, which specifies continuous extraction with reflux condenser, while for the new materials it is required that they be extracted according to 5-B, which specifies extracting by collecting 2 liters of percolate outside, with no reflux extraction. It was suggested that data be submitted for publication in reference to the subject.

(The Editors of the JOURNAL wish to call the special attention of all members to the last two paragraphs of the report of the Council meeting. If anything is to be done in the way of committee work on these two matters, there ought to be a quantity of data presented on which to base the work.)

PROPOSED CHANGES IN METHODS.

The following changes have been proposed in writing to the Secretary in accordance with paragraph 22 of the By-Laws of the A. L. C. A.

(1) That the existing "provisional methods for the analysis of oils and fats" be discontinued as part of the A. L. C. A. methods.

(2) That the existing "provisional method for the color valuation of tanning materials" be discontinued as part of the A. L. C. A. methods. H. C. REED, *Secretary.*

PROPOSED PROVISIONAL METHOD FOR SULPHONATED OILS.

MOISTURE.

Weigh between 30.0 and 40.0 grams (depending on amount of water present) into a flask of 250 to 300 cc. and add 75 cc. water saturated xylol, prepared by heating a mixture of water and xylol with frequent shaking and subsequently removing the water in a separatory funnel. Connect to a Liebig condenser and place flask in a bath of paraffine or a heavy lubricating oil. Distill moderately until the distillate comes clear. Collect distillate in

Digitized by Google

a tube graduated to 1/10 cc. and wash condenser with a stream of xylol from a wash bottle. Place graduated tube in hot water and when the distillate is clear, cool. The percentage of moisture is obtained by dividing the volume of water in the distillate by the weight of oil taken.

NOTE.—For the graduated tube Eimer & Amend's No. 3812 is recommended.

ASH.

Weigh any convenient quantity into a dish or crucible. Ignite gently, allowing the oil to burn and complete incineration until all carbon is consumed.

NON-SAPONIFIABLE.

Weigh approximately 10.0 grams of oil into an 8-ounce Erlenmeyer flask and add 5 cc. aqueous KOH solution (50.0 grams KOH in water and dilute to 100 cc.), 45 cc. ethyl alcohol and a few glass beads. Boil one hour with reflux condenser. Add 100 cc. water and cool. Transfer to separatory funnel and shake at least three times with petrolic ether (B. P. 40° to 75° C.) using 50 cc. each time. Wash ether layer at least three times with 50 cc. water containing 10 cc. ethyl alcohol. Use alcohol to break emulsions. Evaporate ether extract in tared vessel, cool and weigh.

NOTE.—If the contents of the flask bump violently during saponification add 25 cc. petrolic ether, and proceed.

COMBINED SO_3.

(*a*) Weigh approximately 4.0 grams into an Erlenmeyer flask and boil for 40 minutes with 30 cc. HCl (1:5). Shake frequently. Cool, transfer to separatory funnel and shake out with petrolic ether. Draw off aqueous layer and wash ethereal layer with water. Combine washings with main aqueous portion and determine the sulphuric acid as barium sulphate. From the amount thus found, the quantity as determined in (*b*) is subtracted and the difference calculated as SO_3.

(*b*) Dissolve 4.0 grams in ether and shake out several times with 25 cc. concentrated brine free from sulphates. Combine the washings, dilute, filter and determine the sulphuric acid as barium sulphate.

Digitized by Google

TOTAL FATTY OIL.

The total fatty oil shall be the difference between 100 per cent. and the sum of moisture, ash and non-saponifiable.

NOTE.—The results obtained by these methods shall be reported only in one decimal place.

Submitted in accordance with paragraph 23 of the By-Laws of the A. L. C. A.

H. C. REED, *Secretary.*

REPORT OF CHAIRMAN OF COMMITTEE ON COMPARATIVE ANALYSIS.

By Charles R. Delaney.

This report has necessarily been very much delayed, owing to the fact that the Committee on Revision of the Revised Method were unable to submit the proposed changes before October, 1913.

Requests were made to the active members of the Association immediately upon receipt of advices from this latter Committee, inquiring as to co-operation, and 148 requests drew 19 affirmative replies. It was then decided to send out one sample each of ordinary quebracho extract of the usual commercial grade, and a similar sample of refined myrobalan extract. The samples were bottled under proper precautions and sent out to the various collaborators, with a copy of report of the Committee on Revision of the Revised Method, with the following request—that each collaborator would analyze both samples, using the quantity which was specified and report upon the method that was then in use in his laboratory, and then make two analyses using the proposed changes. The results are appended.

The Chairman of the Committee particularly wishes to express to the active members of the American Leather Chemists' Association his opinion that there is altogether too much latitude permitted in the method which is now official, and this same latitude is also allowed evidently by the Committee on Revision, for nothing is said about it, particular reference being made to the Official Method, Page 13, under heading "Analysis of Extracts Cooling, A and B." Is there any particular reason why

Digitized by Google

the slow cooling method cannot be made Standard, and not permit the rapid cooling method at all for Official Analysis? As the writer had occasion to say before, it would be a great deal better for the American Leather Chemists' Association to endeavor to make the errors constant rather than to allow them to be variable, as at the present time, depending entirely upon the whim or practice of the analyst, as the case may be.

Following are reports of analyses:

(In all the tables *s* denotes slow cooling; *r*, rapid cooling; *c*, slow chroming; *d*, rapid chroming; *b*, dried to constant weight.)

TABLE I.—TOTAL SOLIDS.

		Quebracho extract			Myrobalan extract		
Analyst		Method now used	Proposed method	Difference	Method now used	Proposed method	Difference
J. S. Rogers		43.70	43.75	+0.05	42.52	42.37	—0.15
	b				41.66	41.60	—0.06
F. O. Sprague		44.25	44.05	—0.20	42.58	42.63	+0.05
C. C. Smoot, III	*r*	43.82	44.27	+0.45	42.38	42.57	+0.19
	s	44.24	44.29	+0.05	42.78	42.54	—0.24
W. R. Snell		44.15	44.00	—0.15	42.68	42.51	—0.17
A. Schubert, G. W. Toms, Jr	*r*	43.83	43.80	—0.03	42.59	42.63	+0.04
	s	43.70	43.72	+0.02	42.50	42.49	—0.01
G. W. Ellsworth		45.20	44.60	—0.60	44.50	44.50	
F. M. Loveland	*s*		43.96			42.45	
	r		44.05			42.57	
L. A. Cuthbert	*s*	43.70	43.63	—0.07	42.59	42.73	+0.14
	r	43.70	43.63	—0.07	42.77	42.65	—0.12
J. E. McNutt	*s*	43.79	43.62	—0.17	42.65	42.55	—0.10
	r	43.74	43.69	—0.05	42.51	42.45	—0.06
R. H. Wisdom	*r*	43.86	43.88	+0.02	42.72	42.69	—0.03
	s	43.88	43.85	—0.03	42.73	42.77	+0.04
C. W. Norris		43.89	43.82	—0.07	42.56	42.51	—0.05
C. R. Oberfell, L. M. Richeson		43.91	43.85	—0.06	42.68	42.78	+0.10
J. M. Seltzer	*s*	43.88	43.82	—0.06	42.53	42.62	+0.09
	r		43.77	—0.11		42.57	+0.04
T. Blackadder		43.90	44.40	+0.50	42.54	42.71	+0.17
H. H. Hurt		44.30	44.48	+0.18	42.18	42.22	+0.04
S. T. Adair		45.08	44.75	—0.33	42.37	41.94	—0.43
General average		44.03	43.98		42.14	42.58	
Highest		45.20	44.75	—0.60+0.50	44.50	44.50	—0.43+0.19
Lowest		43.70	43.62	—0.03+0.02	41.66	41.60	—0.01+0.04
Greatest difference		1.50	1.13		2.84	2.90	

Digitized by Google

TABLE II.—SOLUBLE SOLIDS.

Analyst		Quebracho extract			Myrobalan extract		
		Method now used	Proposed method	Difference	Method now used	Proposed method	Difference
J. S. Rogers		41.57	41.39	—0.18	40.80	40.84	+0.04
	b				40.13	40.18	+0.05
F. O. Sprague		41.49	41.37	—0.12	41.08	41.47	+0.39
C. C. Smoot, III	*r*	42.30	41.87	—0.43	41.14	41.62	+0.38
	s	42.10	41.77	—0.33	41.18	41.64	+0.36
W. R. Snell		41.14	40.57	—0.57	40.70	40.89	+0.19
G. W. Toms, Jr.	*s*	40.47	40.50	+0.03	40.47	40.54	+0.07
A. Schubert	*r*	41.25	41.19	—0.06	40.73	40.79	+0.06
G. W. Ellsworth		41.20	41.10	—0.10	42.57	42.43	+0.14
F. M. Loveland	*s*		41.14			40.90	
	r		41.41			41.89	
L. A. Cuthbert	*s*	40.83	40.74	—0.07	41.44	41.26	—0.18
	r	42.05	41.42	—0.63	41.46	41.48	+0.02
J. E. McNutt	*s*	41.05	40.95	—0.10	41.19	41.13	—0.06
	r	42.26	41.62	—0.64	41.35	41.43	+0.08
R. H. Wisdom	*r*	42.17	41.44	—0.63	41.49	41.54	+0.05
	s	41.12	40.94	—0.18	41.16	41.26	+0.10
C. W. Norris		40.73	40.78	+0.05	40.80	40.72	—0.08
C. R. Oberfell / L. M. Richeson		40.93	40.92	—0.01	41.50	41.43	—0.07
J. M. Seltzer	*s*	40.92	40.81	—0.11	41.36	41.32	—0.04
	r		40.95	+0.03		41.33	—0.03
T. Blackadder		40.78	41.61	+0.83	40.84	41.17	+0.33
H. H. Hurt		41.95	42.24	+0.29	41.10	41.03	—0.07
S. T. Adair		42.40	42.90	+0.50	41.37	41.00	—0.37
General average		41.22	41.29		41.13	41.22	
Highest		42.40	42.90	—0.64+0.83	42.57	42.43	+0.39—0.37
Lowest		40.47	40.50	—0.01+0.03	40.13	40.18	+0.02—0.03
Greatest difference		1.93	2.40		2.44	2.25	

Digitized by Google

TABLE III.—INSOLUBLE SOLIDS.

Analyst	Quebracho extract: Method now used	Quebracho extract: Proposed method	Quebracho extract: Difference	Myrobalan extract: Method now used	Myrobalan extract: Proposed method	Myrobalan extract: Difference
J. S. Rogers	2.13	2.36	+0.23	1.72	1.53	—0.19
b				1.53	1.42	—0.11
F. O. Sprague	2.76	2.68	—0.08	1.50	1.16	—0.34
C. C. Smoot, III *r*	1.72	2.40	+0.68	1.24	0.92	—0.32
s	1.04	2.52	+1.48	1.60	0.93	—0.67
W. R. Snell	3.01	3.43	+0.42	1.98	1.62	—0.36
G. W. Toms, Jr *s*	3.23	3.22	—0.01	2.03	1.95	—0.08
A. Schubert *r*	2.58	2.61	+0.03	1.80	1.84	+0.04
G. W. Ellsworth	4.00	3.50	—0.50	1.93	2.07	+0.14
F. M. Loveland *s*		3.06			1.31	
r		2.16			1.16	
L. A. Cuthbert *s*	2.87	2.89	+0.02	1.15	1.47	+0.32
r	1.65	2.21	+0.56	1.31	1.17	—0.14
J. E. McNutt *s*	2.74	2.67	—0.07	1.46	1.42	—0.04
r	1.48	2.07	+0.59	1.16	1.02	—0.14
R. H. Wisdom *r*	1.69	2.47	+0.80	1.23	1.15	—0.08
s	2.76	2.91	+0.15	1.57	1.51	—0.06
C. W. Norris	3.16	3.04	—0.12	1.76	1.79	+0.03
C. R. Oberfell / L. M. Richeson	2.98	2.93	—0.05	1.18	1.35	+0.17
J. M. Seltzer *s*	2.96	3.01	+0.05	1.17	1.30	+0.13
r		2.82	—0.14		1.24	+0.07
T. Blackadder	3.12	2.89	—0.23	1.74	1.54	—0.20
H. Hurt	2.35	2.24	—0.11	1.08	1.19	+0.11
S. T. Adair	2.68	1.85	—0.83	1.00	0.94	—0.06
General average	2.55	2.69		1.48	1.37	
Highest	4.00	3.50	+1.48—0.83	2.03	2.07	+0.32—0.67
Lowest	1.04	1.85	+0.02—0.01	1.00	0.92	+0.04—0.04
Greatest difference	2.96	1.65		1.03	1.15	

Digitized by Google

TABLE IV.—NON-TANNINS.

Analyst	Quebracho extract: Method now used	Quebracho extract: Proposed method	Quebracho extract: Difference	Myrobalan extract: Method now used	Myrobalan extract: Proposed method	Myrobalan extract: Difference
J. S. Rogers	8.31	8.27	—0.04	16.01	15.94	—0.07
b				15.94	15.78	—0.16
F. O. Sprague *c*	7.92	8.01	+0.09	15.29	15.26	—0.03
d	8.01	7.87	—0.14	15.49	15.40	—0.09
C. C. Smoot, III	9.01	9.35	+0.34	16.48	16.59	+0.11
	8.85	9.46	+0.59	16.50	16.54	+0.04
W. R. Snell	8.11	8.07	—0.04	15.67	15.54	—0.13
G. W. Toms, Jr.. *c*	7.58	7.58	—0.00	15.37	15.28	—0.09
A. Schubert *d*	7.85	7.81	—0.04	15.50	15.44	—0.06
G. W. Ellsworth	8.44	8.26	—0.18	16.01	15.76	—0.25
F. M. Loveland		8.73			15.94	
		8.73			15.61	
L. A. Cuthbert *s c*	7.88	7.60	—0.20	15.60	15.55	—0.05
r c	7.68	7.65	—0.03	15.37	15.24	—0.13
s d	7.66	7.50	—0.16	15.47	15.31	—0.16
r d	7.61	7.77	+0.16	15.22	15.21	—0.01
J. E. McNutt *s c*	7.82	7.63	—0.19	15.43	15.51	+0.08
r c	7.67	7.68	+0.01	15.43	15.42	—0.01
s d	7.79	7.52	—0.27	15.29	15.41	+0.12
r d	7.62	7.61	—0.01	15.28	15.19	—0.09
R. H. Wisdom *r d*	8.15	8.00	—0.15	15.47	15.42	—0.05
s c	8.08	8.01	—0.07	15.30	15.32	+0.02
C. W. Norris	7.73	7.70	—0.03	15.18	15.22	+0.04
C. R. Oberfell / L. M. Richeson	7.68	7.71	+0.03	15.28	15.26	—0.02
J. M. Seltzer *s c*	7.90	7.86	—0.04	15.22	15.11	—0.11
s d		7.88	—0.02		15.15	—0.07
r c		7.84	—0.06		15.21	—0.01
r d		7.85	—0.05		15.21	—0.01
T. Blackadder	7.99	8.06	+0.07	15.36	15.45	+0.09
H. H. Hurt	7.82	7.87	+0.05	15.07	14.99	—0.08
S. T. Adair	8.35	8.64	+0.29	15.27	15.48	+0.19
General average	7.98	8.02		15.52	15.48	
Highest	9.01	9.46	+0.59—0.27	16.50	16.59	+0.19—0.25
Lowest	7.58	7.50	+0.01—0.01	15.07	14.99	+0.02—0.01
Greastest difference	1.43	1.96		1.43	1.60	

Digitized by Google

TABLE V.—TANNINS.

Analyst	Quebracho extract: Method now used	Quebracho extract: Proposed method	Quebracho extract: Difference	Myrobalan extract: Method now used	Myrobalan extract: Proposed method	Myrobalan extract: Difference
J. S. Rogers	33.26	33.12	—0.14	24.79	24.90	+0.11
b				24.19	24.40	+0.21
F. O. Sprague	33.57	33.36	—0.21	25.79	26.21	+0.42
d	33.36	33.50	+0.14	25.59	26.07	+0.48
C. C. Smoot, III	*r* 33.29	32.52	—0.77	24.66	25.03	+0.37
s	33.25	32.31	—0.94	24.68	25.10	+0.42
W. R. Snell	33.03	32.57	—0.46	25.03	25.35	+0.32
G. W. Toms, Jr. } *c*	32.89	32.92	+0.03	25.10	25.26	+0.16
A. Schubert } *d*	33.40	33.38	—0.02	25.23	25.35	+0.12
G. W. Ellsworth	32.76	32.84	+0.08	26.56	26.67	+0.11
F. M. Loveland		32.17			25.20	
		33.16			25.80	
L. A. Cuthbert *sc*	32.95	33.14	+0.19	25.84	25.71	—0.13
rc	34.37	33.77	—0.60	26.09	26.24	+0.15
sd	33.17	33.24	+0.07	25.97	25.95	—0.02
rd	34.44	33.65	—0.79	26.24	26.27	+0.03
J. E. McNutt *sc*	33.23	33.32	+0.09	25.76	25.62	—0.14
rc	34.59	33.94	—0.65	25.92	26.01	+0.09
sd	33.26	33.33	+0.17	25.90	25.72	—0.18
rd	34.64	34.01	—0.63	26.07	26.24	+0.17
R. H. Wisdom *rd*	34.02	33.44	+0.42	26.02	26.12	+0.10
sc	33.04	32.93	+0.11	25.86	25.94	+0.08
C. W. Norris	33.00	33.08	+0.08	25.62	25.50	—0.12
C. R. Oberfell } L. M. Richeson }	33.25	33.21	—0.04	26.22	26.17	—0.07
J. M. Seltzer *sc*	33.02	32.95	—0.07	26.14	26.21	+0.07
sd		32.93	—0.09		26.17	+0.03
rc		33.11	+0.09		26.12	—0.02
rd		33.10	+0.08		26.12	—0.02
T. Blackadder	32.79	33.55	+0.76	25.48	25.72	+0.24
H. H. Hurt	34.13	34.36	+0.23	26.03	26.04	+0.01
S. T. Adair	34.05	34.26	+0.21	26.10	25.52	—0.58
General average	33.47	33.24		25.64	25.76	
Highest	34.64	34.36	+0.76—0.94	26.56	26.67	+0.48—0.58
Lowest	32.76	32.17	+0.03—0.02	24.19	24.40	+0.01—0.02
Greatest difference	1.88	2.19		2.37	2.27	

NOTES BY COLLABORATORS.

ROY H. WISDOM:—"A comparison of the methods, especially on the quebracho, is to say the least, disconcerting. On the present Official Method, there is a difference in tannin of 0.98 per cent., due entirely to the latitude allowed. It has been

Digitized by Google

proved time and again that rapid cooling has a marked effect on the insolubles item of ordinary quebracho. The reporter admits that he voted for the present Official Method in spite of this fact, but it was only because the method as a whole was a vast improvement on the old one.

"By the Revised Method, the difference in tannin is 0.51 per cent.—the clause calling for first dissolving the extract in 400 cc. water, being responsible for this reduction and equalizing in a measure the effect shown in the present Official Method.

On the myrobalan extract, the difference in tannin by the present Official Method is but 0.16 per cent. as against 0.18 per cent. by the Revised Method. The rapid cooling has the same effect here but to a much less extent.

"From the above results, there is but one conclusion to draw—Too much latitude is allowed by the present Official Method."

J. S. ROGERS:—"In drying the quebracho residues 16 hours was sufficient, but a longer time was required for the myrobalan residues. The proposed changes seem good. The method of making the solutions is better I think than the old method."

F. O. SPRAGUE:—"By way of comment, the analyses of myrobalan extract indicate less insolubles by proposed method of dissolving,—and increase in non-tannins by the slow method of preparing the hide powder. These results are not borne out by the quebracho, however. Results on treating hide powder with water instead of the extract shows one milligram more residue from hide powder prepared by short method than by regular. I have never thought the hide powder quite as insoluble by this short process, and would be more in favor of shaking it for an hour with distilled water rather than the short digestion.

C. C. SMOOT III:—"You will notice that I have used the rapid method of cooling, using old method, and slow cooling on the revised method. As has been the result in all my former work by this means I find that the results are good on the myrobalan extract, but are far from standard on the quebracho. I have invariably found that when dealing with quebracho extracts very rapid cooling or rapid chroming of the hide would not give me comparable results with those obtained by slow cooling and slow chroming methods. In this I know I have not been upheld by

Digitized by Google

the work of other members but this is the consistent value in my laboratory.

GEORGE W. TOMS, JR., ADOLF SCHUBERT:—*"Comment on Liquid Quebracho Extract.*—Both slow cooling methods give practically identical results, so that nothing is gained or lost by either method of making up solutions. Slow cooling shows higher insolubles with a corresponding apparent loss of tan. Both rapid cooling methods give practically identical results. Nothing gained either way of making up. Rapid cooling shows lower insolubles and apparent higher tan content. It seems evident that some provision should be made regarding methods of running analysis on an extract showing high insolubles, there being such a marked difference in the insolubles and tannin content, when made up both ways. Concordant results will not be obtained between analysts if one should put it through by the slow cooling method and the other by the rapid cooling.

"Comment on Liquid Myrobalan Extract.—Remarks regarding making up of solutions on quebracho also apply here. Results more closely comparable on slow and rapid cooling, as insolubles are lower.

"We never knead the hide powder, while washing we simply stir it now and then with a glass rod. Practically no difference in results from rapid chroming of hide by shaking at once, or standing 30 minutes before shaking. Sixteen and six-tenths cc. of N/10 NaOH required to neutralize the equivalent of 10 grams absolutely dry hide, when tested as per directions.

"Wet hide contained 74 per cent. water.

"Our shaking apparatus measures 3½ inches from center of bottle to center of axis, and makes 64 revolutions per minute. Time of evaporation, 16½ hours."

FRANK M. LOVELAND:—"You will kindly note that by the two methods the results are at quite a variance on the tannin content, especially as regards the quebracho. On this extract the trouble lies in lower reds on the rapid cooled, the non-tannins remaining constant. With the myrobalan extract the non-tannins also play a part in the result."

W. K. ALSOP:—"Enclosed you will find tabulated analyses of the samples of extract you sent for collaborative work. These

Digitized by Google

analyses were made by L. A. Cuthbert and J. E. McNutt on the separate samples. These samples were analyzed by the Official Method, both slow cooling and rapid cooling, and also were diluted up in accordance with the proposed scheme in Section 7, A and B, paragraph 1. I do not see that there is anything else in the proposed revision that calls for a separate analysis. Our shaker runs from 60 to 65 revolutions per minute. The size of the bottles we use is as specified, and the centers are 3½ inches from the axis. We do not excessively knead, or work the hide, when washing it. The rapidly cooled solutions of quebracho extract filtered faster than the slowly cooled, and it was impossible to get them as clear. This is something that I have particularly noticed in the case of quebracho extract, when trying out the difference between slowly cooled and rapidly cooled solutions.

"The hide powder for both sets of these determinations was all chromed at once and of course it is only a coincidence that the moisture happens to be the same in the slowly chromed and rapidly chromed hide.

"Two liter solutions were used in all cases instead of one liter, and by the rapid cooling process, it took about one hour to cool them to 20°."

J. M. SELTZER:—"Moisture in air dry hide powder, 12.46 per cent. N/10 NaOH required to neutralize 10 grs. dry hide powder, 12.85 cc.

"It is the opinion of the writer that 400 cc. of water added to the liter flask before washing in the extract is an excessive amount and does not leave enough water to thoroughly rinse the weighing bottle or beaker. In solid extracts there would remain only 400 cc. with which to rinse the beaker. Two hundred cc. of water added to the 1-liter flask and 400 cc. to the 2-liter flasks before dilution would be a more desirable amount to use. The writer is not in favor of prolonging the time for drying residues over 16 hours, but if a broadening of the drying specifications is absolutely necessary the maximum limit should not be over 18 hours. The following experiments were made in order to find out what difference would be caused by a longer period of drying.

Digitized by Google

Time of drying Hours	Quebracho Extract. Total solids Per cent.	Myrobalan Extract. Total solids Per cent.
16	43.81	42.64
18	43.80	42.59
20	43.76	42.23
	Chestnut extract No. 1 Per cent.	Chestnut extract No. 2 Per cent.
16	40.44	36.22
20	40.31	36.12

"While the longer period of drying does not affect the quebracho extract to any marked degree, due to containing a low percentage of sugar, it certainly does affect the extracts containing higher amounts of sugars, such as chestnut, myrobalan, valonia, oak bark, etc."

NOTES ON THE DETERMINATION OF FREE SULPHURIC ACID IN LEATHER.*

By Otto Kress.

[F. P. Veitch, Chairman of the Committee on Leather Analysis, was called on for a report in regard to determination of free sulphuric acid. He said that the net result of tests on the Procter-Searle and other methods had been to convince him that none of the published methods give quantitative results. No collaborative work had been done.]

The object of this paper is not to present any new method for the determination of free sulphuric acid in leather, but to arouse if possible a discussion as to causes of the deterioration of leather especially book-binding leather, and as to the needs of an official method for the determination of free mineral acid.

The causes of the deterioration of leather have been investigated with rather surprising and varying results. The occurrence of free mineral acid, *viz.*, sulphuric or hydrochloric acid, or of oxalic acid, which are the only injurious acids commonly used in the preparing and finishing of leather, have been regarded as the main cause of this decay.

Eitner[1] in his paper on the "Influence of Retained Sulphuric

* Read at the *A. L. C. A.* Convention, Atlantic City, N. J., Dec. 6, 1913, by F. P. Veitch.

[1] *Der Gerber*, 1907, 33, pp. 267-269, 281-283, 296-299, 309-311. *J. S. Chem. Ind.*, 1907, 26, p. 1245.

Digitized by Google

Acid on the Quality of Leather" arrived at slightly different conclusions from other investigators. He soaked oak tanned leather in sulphuric acid and then washed for varying periods up to 48 hours. After 24 hours no further acid was removed, and the remainder 1.1 to 1.2 per cent. was considered as combined with the hide substance. As permissible sulphuric acid content he gave 1 per cent. up to which point he claims the tenacity and quality of the leather appears to be increased. The Wünsch method was used for determining the sulphuric acid.

In the various reports of the committees on leather for book-binding published in the *Journal Society Arts* and in the report of the German Libraries on book-binding[1] the presence of mineral acid, especially sulphuric acid introduced either in the stripping of leather before retannage (East India stock) or in the clearing acid coloring after tannage is given as one of the principal reasons for this deterioration.

The consumers of leather have been taught to regard the free mineral acid as a criterion of the permanence of leather. Such far more important tannery operations as depilating, bating, proper tanning and choice of proper tanning agent (to avoid catechol tannins) and the general mechanical working of the leather are to them of secondary importance. The use of free mineral acid can be avoided in the tannery and organic acid such as formic acid can be and is substituted when necessary.

Unfortunately the chemist required to make the analysis has difficulty in deciding upon a method that will be both rapid and accurate. Most of the methods for determining free sulphuric acid in leather excepting the benzidine method of M. C. Lamb and J. W. Lamb[2] and the magnesium bicarbonate method of B. Kohnstein[3] are I believe fully described with original references in Procter's "Leather Industries Laboratory Book."

The determination of the percentage of free sulphuric acid in leather offers many difficulties not only in the correct sampling

[1] *Der Gerber*, 1911, **37**, pp. 143-144.
J. S. Chem. Ind., 1911, **30**, p. 818.

[2] *Leather Trades Review*, 1904 [930], pp. 25-27.
J. S. Chem. Ind., 1904, **23**, p. 134.

[3] *Collegium*, 1911, pp. 314-317.
J. S. Chem. Ind., 1911, **30**, p. 1174.

Digitized by Google

but also due to errors in various methods. There appears at present to be no simple accurate method for this determination. The various volumetric methods described appear to me to offer too many errors due to substances which may be introduced during conversion of pelt to finished leather. It appeared possible that a method of extracting the acid and titrating using an indicator not affected by organic acid but only by strong mineral acid, such as Töpfers reagent, might succeed; but concordant results were not obtained. The ash of the leather, which is invariably alkaline, is no criterion as to the presence of free mineral acid, nor is the direct action of indicators, such as Congo red.

As the criterion for judging the quality and permanence of book leather seems at present in the opinion of the consumers of such leather to be the percentage of free mineral acid, the method of Balland and Maljean,[1] which appears from the literature of this subject to be the one most commonly used, was tried out as follows:

Samples of 2-5 gr. shredded leather were treated in a platinum dish on the water-bath with a solution of sodium carbonate and evaporated to dryness. This treatment was repeated then ashed at low heat and extracted by dilute hydrochloric acid in the ordinary way for determining sulphates by barium sulphate precipitation.

A blank of 2-5 gr. was directly incinerated in a platinum dish and sulphates determined gravimetrically as barium sulphate.

According to theory the actual percentage of sulphuric acid is of course the difference between total and blank.

The results by this method as are to be expected will be high as in the ignition in presence of alkali all sulphate sulphur will be retained and probably a part of the organic sulphur will be oxidized and held as sulphate.

In the blank the organic sulphur is lost and sulphates such as calcium and iron sulphates may in the absence of alkali and depending on the conditions be reduced to sulphide and oxide with consequent loss in sulphate.

The method which appeared to be the most satisfactory was

[1] *Comp. Rend.*, 1894, pp. 119, 913, 915.
J. S. Chem. Ind., 1895, 14, p. 496.

Digitized by Google

also tried, *viz.*, the method of Jean[1] which consists in extracting in a Soxhlet 8-15 gr. shredded leather with *absolute* alcohol, placing in the flask some dry sodium carbonate to neutralize the free sulphuric acid extracted. After complete extraction the alcohol was evaporated. Organic matter was destroyed by ignition in platinum and sulphates determined in usual way. The leather samples were only air dried to avoid forming a hide sulphuric acid compound that might not be extracted by alcohol.

The following determinations were simply made as routine analyses with no intention of publishing the results. This will account for incompleteness of data.

Sample	Balland and Maljean Alkaline method	Jean Absolute alcohol extract
I.—*Red Morocco*	0.456% total	0.055% H_2SO_4
	0.16% blank	
	0.296% free H_2SO_4	
II.—*Black Glazed Sheep*	0.99% total	0.36% H_2SO_4
	0.29% blank	0.35% H_2SO_4
	0.70% free H_2SO_4	
III.—*Grey Suede*	0.88% total	0.11% H_2SO_4
	0.10% blank	0.11% H_2SO_4
	0.78% free H_2SO_4	
IV.—*Green Morocco*	0.31% total	0.06% H_2SO_4
	0.09% blank	
	0.22% free H_2SO_4	
V.—*Tan Pig Skin*	0.37% total	0.046% H_2SO_4
	0.06% blank	
	0.31% free H_2SO_4	
VI.—*Brown Morocco.* No H_2SO_4 used in any operation	0.42% total	0.04% H_2SO_4
	0.02% blank	0.04% H_2SO_4
		0.05% H_2SO_4
	0.40% free H_2SO_4	0.07% H_2SO_4
		0.04% H_2SO_4
VII.—*English Skivers.* Received at tannery pickled in NaCl and H_2SO_4. Tanned, using H_2SO_4 in tanning bath. Analyzed in tanned condition		0.05% H_2SO_4
		0.046% H_2SO_4

[1] *Revue Chim. Analyst*, 1895, pp. 3, 13.

Digitized by Google

Sample	Balland and Maljean Alkaline method	Jean Absolute alcohol extract
VIII.—*New Zealand Skivers.* Received two picklings. Tanned using H_2SO_4 and analyzed after tannage		0.057% H_2SO_4 0.05% H_2SO_4 0.05% H_2SO_4
IX.—*English Pickled Lamb Skins* (not split). Received pickled. Tanned, using H_2SO_4, dyed and finished, then analyzed		0.07% H_2SO_4 0.05% H_2SO_4
X.—*Red Sudan Goat.* Received in tanned state. Analyzed direct		0.006% H_2SO_4
XI.—*Yellow Sudan Goat.* Received in tanned state. Analyzed direct		0.015% H_2SO_4
XII.—*East India Goat.* Stripped, using H_2SO_4. Retanned, dyed and finished, then analyzed	0.83% total 0.10% blank 0.73% free H_2SO_4	0.09% H_2SO_4 0.12% H_2SO_4
XIII.—*Brown East India Goat.* No sulphuric acid used in stripping. Retanned and finished, then analyzed	1.05% total 0.11% blank 0.94% free H_2SO_4	0.13% H_2SO_4
XIV.—*East India Goat.* Up country tannage. As skins are imported. Nothing done to them in tannery	0.11% total 0.05% blank 0.06% free H_2SO_4	
XV.—*East India Goat.* Madras tannage. As skins are imported. Nothing done to them in tannery	0.16% total 0.03% blank 0.13% free H_2SO_4	

Digitized by Google

Sample	Balland and Maljean Alkaline method	Jean Absolute alcohol extract
XVI.—*East India Goat.* Madras tannage. Same as XV, only stripped. Retanned and finished. No H_2SO_4 used in tannery	0.42% total 0.04% blank 0.38% free H_2SO_4	
XVII. *Sultan Red Calf Finish Persian.* Skins were stripped (using no H_2SO_4). Retanned and finished.....		0.08% H_2SO_4
XVIII.—*Powder Grain Seal* (black). Skins received in hair. No sulphuric acid used in tannery	0.60% total 0.26% blank 0.34% free H_2SO_4	
XIX.—*Black Dull Seal.* Received in hair. No sulphuric acid used..	0.64% total 0.27% blank 0.37% free H_2SO_4	
XX.—*Black Goat* (Spanish). Leon Spanish goat. Came in hair, flint dried. No H_2SO_4 used at tannery. Analyzed after finishing	1.04% total 0.16% blank 0.88% free H_2SO_4	0.06% H_2SO_4 0.07% H_2SO_4

The results by the alkali method (Balland and Maljean) run from 2 to 11 times as great as by the absolute alcohol (Jean) extraction, depending upon the particular leather examined. With an average for 10 leathers in which determinations were made by both methods, the alkali method gave approximately 6 times the quantity found as by direct extraction.

The first 5 leathers, whose history is not known, were of foreign manufacture and guaranteed free from injurious mineral acid.

The results on the pickled stock after tanning is surprising with regard to the small amount of acid retained even though sulphuric acid was used in the tanning. The difference between

Digitized by Google

the Madras goat before and after retannage and finishing is also surprising as no acid was used in stripping or coloring.

There can be no question that any free mineral acid used in stripping, clearing or dyeing is injurious to leather, but it appears to me that the decay of leather is not primarily due to the small percentage of free acid found. In cases where no sulphuric acid was used in the tanning and finishing, a small percentage of material yielding sulphate on ignition was found to be extracted by the alcohol.

From these peculiar and interesting results, obtained on a few samples of leather, and in consideration of the importance placed by the consumer of limited chemical training on the presence of small amounts of free mineral acid, it appears that it would be of value to have an official method for this determination. This can be the only excuse for this very incomplete paper, as nothing original is presented except that until we have an official method different investigators will not get concordant results unless by chance they use the same method.

DISCUSSION.

MR. J. S. ROGERS:—The work that I have done has been mostly by the Procter-Searle method, and I am very sorry to say that I really haven't any faith in the method. One of the things that I ran across the other day that perhaps will be interesting, is this: that a pure sulfonated oil,—treated by the Procter-Searle method,— gives quite a decided percentage of acidity.

I have not tried the other methods, with the possible exception of an alcohol extraction method which I tried two or three years ago, and I found that the amount of acid extracted was less than the actual amount there.

It seems to me that it would be helpful to everyone concerned if the other people who have done work on the determination of acids in leather would give us their experience. I am sure I would be glad to hear the experience others have had with any method they have tried. I have tried out several different methods that suggested themselves to me, but I have not been able to find anything that was satisfactory.

Digitized by Google

MR. VEITCH:—I might say, Mr. President, that we are often asked to make this determination for the Government printing office for their book leathers. In fact we are doing it all the time; and we have gotten to the point where we are afraid to say much. All we can do is to report an acid reaction. We are afraid to make any attempt to report quantitatively. Now that is decidedly unsatisfactory, because we do not know how harmful small quantities are or whether or not they are harmful. We can so far only reason by analogy that small quantities would be harmful, but slightly harmful possibly. I would say that Mr. Rogers has treated a number of pieces of leather with different quantities of sulphuric acid. The effect of that treatment is clearly seen with percentages over 4, I think. Mr. Rogers, is that right?

MR. ROGERS:—Well, I don't know that we can quite see the effect with 4 per cent. yet, but up to as high as 6 per cent. we can see it decidedly.

MR. VEITCH:—That is just in a few months. Smaller quantities than 6 per cent. have not visibly so far affected the leather.

MR. FAUST:—I would like to ask Mr. Rogers whether he found higher or lower results by using the absolute alcohol.

MR. ROGERS:—Well, I have used it but very little, but the experience that I had was that I got slightly lower results; but as I say I have used it but a very little.

MR. FAUST:—My idea was just the opposite.

MR. ROGERS:—Well, it undoubtedly would extract some of the sulphates.

MR. FAUST:—I was wondering whether the Procter-Searle method could be worked out with the alcohol solution.

MR. ROGERS:—I should think that that would have a decided advantage over the Procter-Searle method, provided you can extract all of your acid.

MR. BALDERSTON:—I would like to ask Mr. Veitch whether the sulphur which is actually present in hide can be responsible for sulphuric acid in the leather. For instance, I have a piece of chrome leather at home which has never been touched by sulphuric acid at any stage of manufacture. If I analyzed that would I find any free sulphuric acid in it?

Digitized by Google

MR. VEITCH:—I cannot answer that except possibly in this way, that we have tested many leathers that we are confident have no acid in them, and find the ash is alkaline by the Procter-Searles method; and I think it is the consensus of opinion of those who have looked into it that the sulphur of the leather does not appear in this reaction to make sulphuric acid.

The other question, about the extraction of free sulphuric acid—I think that, in England, where a good deal of work has been done, the conclusion has been reached that absolute alcohol does not extract all the free sulphuric acid.

ESTIMATION OF FREE SULPHURIC ACID IN LEATHER.*

PREPARATORY STATEMENT.

By Prof. Dr. Johannes Paessler.

In using neradol D, the new tanning material produced by the Badische Anilin und Sodafabrik, the usual quantitative means for determining the free H_2SO_4 in the leather give incorrect results. Neradol D itself, in contrast to the natural vegetable tanning materials, contains sulphur compounds which are also taken up in the tanning process. It must be admitted that under these circumstances those methods of investigation which show the free sulphuric acid from the total sulphuric acid content of the leather necessarily yield too high results. Modern quantitative experiments are, however, based on this.

Therefore it has been shown necessary, since the introduction of neradol D into tanning, to fix a new method of determining the free H_2SO_4 in leather. The experiment station is now at work on a method suited to present conditions and will report on it shortly.

* *Collegium*, 524, 1913, pp. 648-49.

Digitized by Google

DISCUSSION OF THE REPORT ON SAMPLING.*

[C. W. Norris, in presenting his report, which had been published in the December JOURNAL, added a third proposal in regard to the sampling of solid extracts. As the discussion relates chiefly to the proposal to change the method of sampling these extracts, we print here the present method, and the three new proposals.]

PRESENT METHOD.

When carload lots, or less, of bags are to be sampled, 7 per cent. of the number of bags shall be sampled. When shipments of more than a carload and less than 2,000 bags are to be sampled, 20 bags shall be sampled. When shipments of more than 2,000 bags are to be sampled, 1 per cent. of the number of bags shall be sampled.

When 70, or less, barrels are to be sampled, 10 per cent. of the number of barrels shall be sampled. When from 71 to 140 barrels are to be sampled, 9 per cent. of the number of barrels shall be sampled. When from 141 to 210 barrels are to be sampled, 8 per cent. of the number of barrels shall be sampled. When from 211 to 280 barrels are to be sampled, 7 per cent. of the number of barrels shall be sampled. When from 281 to 350 barrels are to be sampled, 6 per cent. of the number of barrels shall be sampled. When from 351 to 420 barrels are to be sampled, 5 per cent. of the number of barrels shall be sampled. When from 421 to 500 barrels are to be sampled, 4 per cent. of the number of barrels shall be sampled. When more than 500 barrels are to be sampled, 3 per cent. of the number of barrels shall be sampled.

PROPOSALS FOR A NEW METHOD.

Proposal (A). The number of packages to be sampled out of a given lot shall be ascertained by taking a percentage of the total number of packages obtained in the following manner: Divide the total number of packages by 100; multiply by 0.02 and subtract from 4. (This is precisely equivalent to dividing by 5000 and subtracting from 4.—ED.)

Thus: $4700 \div 5000 = 0.94$

$4 - 0.94 = 3.06$ per cent.

3.06 per cent. of $4700 = 144$ packages.

* At the *A. L. C. A.* Convention, Atlantic City, Dec. 6, 1913.

Digitized by Google

Provided that for lots of 200 packages and under, 5 per cent. of the number of packages shall be sampled, and for lots of 10,000 packages or over, 2 per cent. of the number of packages shall be sampled.

Proposal (B). For every shipment of extract to be sampled the number of packages shall be 14 for every 50,000 pounds or less, except that for lots of 200 packages or under, 5 per cent. of the number of packages shall be sampled.

Proposal (C). On units of weight of 50,000 or less, the number of packages to be sampled shall be represented by 3 per cent. of the weight.

DISCUSSION.

MR. DELANEY:—Mr. Chairman, there is a statement in there, "Sampling at place of manufacture shall be conducted by running a portion from the middle of each strike into a mold holding at least two pounds." We have found in manufacturing solid extract that a sample from the middle of a strike will not represent a fair average of the strike, for this reason, that there is invariably a certain amount of steam in the pan from which the strike is running and there is always a certain amount of evaporation that is going on. That amount of evaporation is not so great for the first half but it is considerably greater for the last half. Now I do not know whether other manufacturers of solid extract run their strikes as we do, but we generally run out about 6 tons at a time, and if we take a sample from the middle of the run it will vary greatly from a sample that is taken just before the end of the run, and what we generally do is this: We take a sample after the run has been going out for a short time, let us say about a quarter of it has gone out. Then we take another sample, running it into the same mold, just before the end of the running out of that particular strike. I simply submit that for your information. It would not be as accurate, as far as we can tell, if we were to take a sample from the middle of the strike as it would taking two samples, one at the beginning and one at the end.

MR. NORRIS:—The section to which Mr. Delaney refers has not been changed; it is just as it was; however, it might be well to take note of what Mr. Delaney says.

Digitized by Google

MR. REED:—Mr. Delaney, does the sample at the first of the run contain more moisture than that at the middle of the run?

MR. DELANEY:—Oh no; but the sample in the middle of the run will contain more moisture than the general average of the entire. The change from the first quarter to the second quarter is hardly noticeable, whereas from the second to the third quarter is very distinctly noticeable. There will be sometimes as much as 1 per cent. difference, because there must be a certain amount of steam used to prevent the "freezing" of the extract.

MR. REED:—My experience has been you are apt to get more moisture at the last of the run than at the middle or the first.

MR. DELANEY:—A difference in manufacture, perhaps.

MR. REED:—The condensation no doubt falls back into the extract, and you really get more moisture in the very last than you do in the first of the strike.

MR. DELANEY:—We don't. We have a big aperture at the top for conducting the vapors away; and I do know that it is my practice to take the first and third sections rather than the middle, for I have found that the middle is not correct. That is only my own experience, and I wanted to make that statement.

MR. GRIFFITH:—I should like to ask Mr. Norris whether the committee have secured any facts and figures which would go to show that the new proposed method is any advantage over the method now in operation. I take it that the old method has worked fairly well and is the most accurate procedure in the science of our industry, and before we proceed to make a change I should like to ascertain what the facts are with regard to the present method in its relation to the proposed method.

MR. REED:—I might cite just one little instance. The old method says, "When carload lots, or less, of bags are to be sampled, 7 per cent. of the number of bags shall be sampled." Well, say we have a 400-bag carload; that is 28 samples; and it goes on to say, "When shipments of more than a carload and less than 2,000 bags are to be sampled, 20 bags are to be sampled." You may have just under 2,000 bags, and you sample 20 bags; and for 400 bags you sample 28 bags. Do you think that is right, Mr. Griffith?

Digitized by Google

MR. GRIFFITH:—Not at all, but the first method does not offer any better solution. You have a formula here which if you carry it on will give you no sample at all.

MR. REED:—Not at all. You have not read the method. You will find that for 10,000 bags and over, 2 per cent. shall be sampled.

MR. GRIFFITH:—Wherein would that be any advantage over the present method? What I want to find out is the truth of the matter. Have you any facts which would go to show that if you do sample 2 per cent., that in the law of averages you get a more equitable result than you are getting now?

MR. REED:—I have just cited you an instance of it, Mr. Griffith. If you will work that out along the same lines I have spoken of, by the old method, you will see that when you have a larger number of packages to be sampled you will get a smaller number of bags. Now that is not true of this proposed method.

MR. GRIFFITH:—But I am talking about the ultimate result, which is the analysis. The sample is two-thirds of the analysis—in moderation. Now an analysis would be challenged just as much by the tanner under this proposed method as it is under the present method, because you do not prohibit the tanner or the consumer from challenging an analysis. That is his right.

MR. REED:—You are speaking now on the question of the number of analyses?

MR. GRIFFITH:—Yes.

MR. REED:—You will find by this method that there are more analyses made than by the old method.

MR. GRIFFITH:—Exactly.

MR. REED:—And more analyses would mean greater accuracy in the result.

MR. GRIFFITH:—Have you anything to prove that?

MR. REED:—Only the general law that the greater number of analyses will give you nearer the true result.

MR. GRIFFITH:—That is an assumption. Have you any facts?

MR. REED:—I don't think any of us need any facts on that proposition.

MR. GRIFFITH:—That is your own opinion, but when it comes down to practice it has been found that samples taken from a

Digitized by Google

shipment, and where that shipment has been distributed afterwards in carloads, and where those carloads in turn have been sampled, that the average of the carload samples has compared very closely with the samples taken from the original shipment.

MR. REED:—That may be, but that does not obviate the statement that two analyses are more accurate than one.

MR. GRIFFITH:—Not at all, but what I am arguing about is that before you change a method I think it is in common fairness to our Association as a whole—not to any particular interest, you understand. I am just as anxious to get the truth of the matter as anybody here—but as an association, as a body of scientists, let us know what we are about before we do it. Now I ask the committee which is proposing changes,—What is the evidence against the present method? Now that is a fair question. I suggest that they ought to have those figures. They ought to be able to prove their contention that the greater number of analyses would make for greater accuracy. But you would still be up against the proposition that you cannot prohibit the tanner from challenging the analysis. You are going on the assumption that the last word is spoken when the analysis goes to the tanner. That is not so.

MR. REED:—I don't see what right you have to make that as an assumption. The tanner always has the right to challenge any analysis. Is that not true?

MR. GRIFFITH:—That is what I said. That is the statement I made.

MR. REED:—And you cannot make any method of sampling or of analysis that will prevent him from having that right.

MR. GRIFFITH:—Exactly. That is my contention. I supposed that was the statement I made; but my point is that we are trying to get at the facts. What are the facts here?

MR. REED:—I will confine my statement simply to this, that I do not believe anybody can dispute the fact that two analyses are better than one.

MR. GRIFFITH:—Well, as the analysis depends on the sample, of course it returns you to the sample again. Now you know you can get two analyses from one carload that are very, very different. The whole object of sampling is to get a sample

Digitized by Google

which will represent the moisture content, because I think the method of analysis, so far as tannin analysis is concerned, gives very concordant results. If you take any number of analyses you will find that, if there is any difference in the tannin content it is reflected in the moisture.

MR. FAUST:—In answer to Mr. Griffith, wherein the committee will try to show the advantage of the new method,—assume a lot of quebracho extract, 5 cars, 2,000 bags. Under the old method you cut 20 bags, draw the sample and analyze it. Under the new method you draw 5 samples cutting probably in the neighborhood of 70 or 80 bags altogether,—14 to 16 bags, or 18 bags, for each sample, having 5 samples, making 5 analyses of those 5 cars. Now it seems to me that it is a self-evident fact that those 5 analyses are going to be more near the truth than that one analysis of just 20 bags; and as far as that goes—there were some figures furnished here on analyses of several carloads of extract showing the difference between maximum and minimum. Now in a case where a shipment of 5 cars of extract is going to several different tanneries, the man who is getting the low car, in case there is that difference, will certainly complain.

MR. GRIFFITH:—Well, this points to the fact that tanners have been laboring under a very great injustice for a considerable time, for the method has been operating now for a number of years and it is extraordinary that we should suddenly discover that he has not been treated fairly.

MR. FAUST:—Oh, it is not as bad as all that. We all want to improve the methods, and I think we can improve the accuracy of the samples by these methods.

MR. GRIFFITH:—I am quite in favor of improving anything, Mr. Faust, but I think in common fairness you ought to be able to produce facts to show that where you increase the number of samples and the analyses at the same time, you have removed an error which exists under the old method.

MR. ALSOP:—It seems to me this is a question that tanners who buy the solid extract ought to have something to say about. According to the old method, as I understand it, a large lot of extract was sampled and then smaller shipments made from this lot, and the analyses of the whole lot has been used to cover

Digitized by Google

these small shipments; and the question is whether the tanners who buy the extract want to have changes made such as are suggested which would involve many more analyses. I think it would be well to hear from some of them.

MR. VEITCH:—I agree with your last statement, Mr. President. I think the tanners chemists here ought to let us hear from them on this subject. In default of their statement we have to assume that this report, very carefully worked out, is the last word of the Association. It seems to me we ought to hear from the tanners' chemist. Is this procedure in agreement with their wishes? Do they agree with it? We ought to have some public statement about it, it seems to me.

MR. NICHOLS:—Has there been any work done on this new process of sampling? Have there been any analyses made to show exact differences, as Mr. Griffith has stated, between the new and the old method? Have we any evidence to show these? Of course we can assume that taking more samples and making more analyses you will have more correct results—it looks as if we should.

MR. REED:—You believe it to be true, do you not, Mr. Nichols?

MR. NICHOLS:—It looks reasonable that the more samples you have taken and the more analyses you have made, the more accurate results you ought to get, although you might get just as good results if the samples are carefully taken. Having each car tested would probably be most accurate and would give the tanner better protection.

MR. OBERFELL:—It does seem to me that it is a fair proposition to the tanner that he should have each carload of extract that he buys analyzed. He buys some extract which may be taken from a larger lot; maybe three or four other tanners have received extract from that same lot, and a comparatively small sample has been drawn representing the portion that he received. It seems to me it is the only tanning material which is sold on which a sample is not taken for each individual shipment. As I understand, tank cars of liquid extract are always sampled. Why should there be an exception in the case of solid extract, unless it is impracticable to take the sample at the place where the

Digitized by Google

extract is brought from abroad and reloaded onto the cars to be shipped to the tanner?

MR. NORRIS:—I will say that the reason it has not been done is just as Mr. Oberfell suggests—the conditions existing heretofore have not permitted it.

MR. DELANEY:—Could Mr. Reed tell us about the usual number of strikes of solid extract that go into one single car?

MR. REED:—Well, I don't know that I can tell you exactly. There may be, as I understand it, as many as 10 strikes in a carload shipment, say, of solid quebracho in bags—as many as 10 strikes in a carload. Now say there are 400 bags—for purposes of comparison—in a carload. That would make 50 strikes in a 2,000 bag lot. Under the present ruling we take 20 samples out of the 2,000 bags. Uder the new ruling I think it is something like 70. Surely under those circumstances and according to the law of averages we would be more likely to strike a fair sample by taking 70 bags than 20 bags.

MR. DELANEY:—There is another thing I would ask Mr. Reed to tell us. About what is the general variation in moisture in extracts as struck from the pan?

MR. REED:—Solid extracts?

MR. DELANEY:—Yes.

MR. REED:—The average variation in moisture—why, it might be, I suppose, 5 per cent.

MR. VEITCH:—What is the maximum?

MR. REED:—I should have said the maximum is about 5 per cent. The average would be 2½. You see it can vary roughly speaking from 75 total solids to 80 total solids. I have seen it vary that much.

MR. LEVI:—We have had a great deal of trouble in sampling our extracts and different things we use in the tannery on account of the samples not being taken properly, so we have appointed one of our chemists as official sampler, and no sample is drawn unless it is in his presence and under his direction. If we get a shipment of say 10,000 bags of quebracho in, a thousand of those bags are put on the warehouse floor. From that thousand bags we take 100 bags and draw the sample for our first analysis. After that, day by day he takes 100 bags and makes analyses of

Digitized by Google

the remaining 900 bags. In that way 10 analyses are made out of the 10,000 bags. We find by that method we can get better results than we ever had before. Of course as long as the extract lies in the warehouse, if the warehouse happens to be damp, there will be a variation. That is, the 10 per cent. sample we draw is put in the warehouse and put aside, and each 100 bags of those thousand bags are sampled by our official sampler and analyzed; and when we come down to the 9,000 bags which are left over, and we take, say, 200 bags to dissolve and use in the tannery, 10 per cent. of those 200 bags are taken again and re-analyzed to find out if our warehouse conditions are exactly right and proper for the storage of that material. It has been a great problem and we hope to have it solved by appointing this official sampler and requiring that no sample shall be taken except by him or directly under his supervision.

MR. REED:—Doctor Levi, the present methods here call for the sampling of 100 bags out of a 10,000 bag lot,—1 per cent.

MR. LEVI:—Out of 10,000 bags 1,000 bags are laid aside.

MR. REED:—Well, the present method says 1 per cent. Do you think that is sufficient?

MR. LEVI:—No; we take 1,000 bags.

MR. REED:—The new method would call for 2 per cent., that is 200 bags. You would consider that an improvement surely over 100 bags?

MR. LEVI:—Oh yes; there is no doubt about it.

MR. NORRIS:—Doctor Levi, do you find any great difference between the different lots of extract? Say you get in 10,000 bags, do you find any great difference between the different lots of 1,000 bags each that you have sampled?

MR. LEVI:—Not very much. Once in a while you do. It depends on how the stuff is shipped. If the lower part of the bag is wet and then dried out, you will find a difference, but we have not found any appreciable difference so far.

MR. NORRIS:—Well, that is one reason why I do not believe that the tanner loses out on a year's contract in taking the analyses of the extract as it has been sampled. There has been considerable fault found, I understand, but I cannot see the cause of it myself. I have had a number of years of experience

Digitized by Google

in sampling extract on the docks, and I think that on a year's contract the tanner gets everything that is coming to him.

In regard to sampling extract at the tannery: A short time ago I was called to a tannery to sample some extract which I had previously sampled on the docks and I inquired as to how they sampled the extract at the tannery. I found that the chemist at that tannery had gone to the superintendent of the tannery to get a man to do the sampling for him. Well, he got the man who happened to be available at that time and it happened to be a Polack. The chemist set the Polack to work sampling the extract and he went back to his laboratory and left the Polack to complete the sampling of the extract. Well, the consequences were that that sample did not check up with my laboratory sample and I think there were very good reasons for it,—simply because there was not a competent man at the tannery to sample the extract.

MR. GRIFFITH:—I should like to ask Dr. Levi whether he found in checking up his analyses that the difference ever exceeded 1 per cent.

MR. LEVI:—What—in tannin?

MR. GRIFFITH:—Yes, in checking up.

MR. LEVI:—No.

MR. GRIFFITH:—Well, that is the basis of my contention, that the present method has answered practically the purpose, and until we can prove to the contrary I do not think we ought to change. I am just as willing to change—I am willing to go down to one bag, if you want to carry the thing to the logical end, take a sample from every bag—but what purpose does it serve from the point of view of the tanner? because we are all trying to help out the tanner.

THE INTER-RELATION BETWEEN THE AMERICAN LEATHER CHEMISTS' ASSOCIATION AND THE NATIONAL ASSOCIATION OF TANNERS.*

By Cudworth Beye.

In the Fall of 1910 in the City of Chicago was held what was then considered a very remarkable gathering. It was pointed out

* Read at the *A. L. C. A.* Convention, Atlantic City, Dec. 6, 1913.

Digitized by Google

that 10 years prior to that time such a gathering would have been absolutely impossible. It was considered that during the short space of 10 years the feeling in favor of a scientific control of tannery establishments had become quite marked. I believe that, whether as a result of that gathering or because of other natural causes, this feeling has become even more a thing of fact, and that the profession of leather chemist to-day is a reality in the minds of the tanners.

Whether or not the interest which the tanner has taken in this American Leather Chemists Association is all that could be hoped for, I believe that the interest which *is* being taken is indicative that your work is recognized as absolutely essential to the best interests of the industry, and therefore should be supported. But I do not feel that the work of the American Leather Chemists Association should be considered as something separate and apart from the work of the tanners themselves. I believe that there should be a closer affiliation between the American Leather Chemists Association and The National Association of Tanners. Something more than that we over here on this side of the footlights approve and applaud the efforts of you over there on the other side. Let us so far as possible be on the same side and work together to the same end. Let the tanners at least be the scene-shifters if that is all we are good for in this particular branch of the work being done for our great industry.

There is at least one agency for bringing this about. It had its birth 3 years ago when under the auspices of The National Association of Tanners a Tanners Institute was permanently established at Brooklyn. Subscriptions were taken for part of the support of this new institution. The subscriptions have been not exclusively from tanners. Many of your members or concerns (not tanners) with whom your members are identified are regular subscribers to the Tanners Institute Fund, thus cementing the two associations together so far as a common financial interest can do it.

There is appointed each year an advisory committee to Tanners Institute with duty to give advice on its own initiative or upon request from Tanners Institute, as to the proper conduct of the

Digitized by Google

school. This committee is appointed by the President of The National Association of Tanners, but the American Leather Chemists Association is privileged and invited to appoint members of its body to work with and be a part of that committee. Here then is additional means whereby our two associations can work together and on a proposition which is essentially of equal interest to both.

And further:—You all know that at Tanners Institute by virtue of a portion of Tanners Institute Fund set aside for that purpose, certain investigations are conducted each year on matters suggested by the School and approved by the Advisory Committee. You have in your hands sets of reports of work which has already been done, which Dr. Rogers undoubtedly will take up with you when I am through. These reports are distributed to a mailing list which has been developed from time to time, and which should include every one of your membership. These reports are sent out to be not only read but in the hope that they be analyzed, discussed, and criticised in the minutest detail. I believe I voice the sincere desire of Tanners Institute and of Dr. Rogers under whom these investigations have been conducted, when I invite you to consider these reports literally as above suggested. I believe I voice Dr. Rogers' feelings when I state that it is a heartless task to perform a duty, whether it is well or poorly done and at the end receive no comment thereon either pro or con. I believe that I also express Dr. Rogers' views when I state that there is no assumption in presenting these reports that they are absolutely accurate either as to methods indicated or as to results and conclusions. Your criticism is sincerely invited. Your discussion is urgently, I wish I might say demanded, for it is only through sincere and helpful criticism and discussion of these reports that they can become of maximum value, and that the school can become of maximum worth to the industry.

It would be a very fine thing should the American Leather Chemists Association at its annual meetings set aside a certain portion of its valuable time for a detailed discussion of these reports which are to be issued each year and I trust that some action may be taken here, to the end that this plan will be

Digitized by Google

adopted. The reports could be printed in your JOURNAL if that would be of any advantage.

I bring to you to-day an invitation from the officers of The National Association of Tanners to hold your next annual meeting in the City of Chicago, at the time that the annual meeting of our Association is held. In issuing this invitation our officers realize the difficulties from your point of view in making such an arrangement, but they feel that the good which would develop from such an arrangement would offset any disadvantages. We earnestly hope that it may be the pleasure of the members of the American Leather Chemists Association here in meeting assembled to vote to accept the invitation hereby tendered. Our President, Mr. John E. Wilder, asks me to express to you his hearty greetings and his hope that it may be so ordered.

DISCUSSION.

Mr. Hurt wished that the Association should do everything in its power to cultivate more intimate relations with the National Association of Tanners, and he offered a resolution, which was seconded by Mr. Reed, and carried, as follows:

Resolved: That we as an association, should do all we can to further the interests of the tanning school at Pratt Institute. Mr. Veitch said that it had always seemed to him very desirable to have more of our meetings held at the same time that the tanners have their meetings, so that tanner and chemist could get into closer touch. A part of the time might be devoted to joint meetings.

Mr. Kerr thought that meeting in Chicago would diminish the attendance of chemists. Mr. Reed suggested that by extending the time of the meeting to four days, the benefit of the joint meeting might be secured without too much crowding. In answer to a question, Mr. Beye said that the National Association of Tanners is obliged to meet in Chicago. He reminded members that the National Association of Tanners were only asking the chemists to come to Chicago once in 4 years. Mr. Veitch thought that by holding longer sessions the business could be accomplished without an extra day. Mr. Alsop remarked that

Digitized by Google

if the Association is to broaden its work by taking up the problems of leather manufacture, it will be necessary for us to cultivate closer relations with the tanners, which could be accomplished by getting into closer relations with the Tanners Association.

Mr. C. R. Delaney brought up the subject of the committee appointed a year ago to consider the subject of forming an American board of arbitration to take cognizance of disputes between foreign shippers of tanning materials and buyers in this country. Mr. Haley replied that he as chairman had selected a committee of five associate members, all tanners, but that several attempts to get the committee together had all failed. The interests of tanners was focussed on events at Washington. He did not think that interest in the subject had been entirely lost, but hoped that the committee might yet get the matter before the National Association of Tanners. It is a subject of greater interest to the associate members of this Association than to the active members, and it is the first opportunity which has been given the associate members to take an active part in the proceedings of this Association. Mr. Haley believed that the negligence of the committee had been due entirely to the extraordinary circumstances which arose during the year.

Mr. Haley proposed a resolution to the effect that it is the sense of the Association that the next annual meeting shall be held in Chicago, at the time of the meeting of the National Association of Tanners, and that at least one day of the meeting be devoted to matters of interest to associate members of this Association. Mr. Smoot seconded the motion. In answer to a question, Mr. Beye said that the tanners' meeting would probably occupy one day, Friday, and suggested that Mr. Haley's motion be amended so as to read "one session" instead of "one day" to be devoted to matters of interest to associate members. Mr. Haley was willing to accept the amendment, saying that the purpose of his motion was to do something to further the interest of the associate members in the Association. He was willing to go further, and support a proposition to extend to associate members the right to vote, except perhaps on technical points. Since the associate members are really the backers of the

Digitized by Google

Association, we must get their active interest if we are to go forward. Mr. Hurt moved that Mr. Haley's motion be so amended as to read, instead of "one day," "such time as may be deemed necessary" for the consideration of matters of interest to associate members. This amendment was accepted by Mr. Haley, and the motion as amended was carried.

DISCUSSION OF COMMITTEE REPORT ON OILS AND FATS.*

After C. R. Oberfell had presented the report of the Committee (published in the December JOURNAL), H. C. Reed asked in reference to the xylol distillation method for determination of water in sulphonated oils whether the xylol which distills over is still saturated with water. Mr. Oberfell in reply quoted Dean's statement that the error due to this cause is not likely to exceed 0.03 per cent., and said that he is in the practice of using again the xylol which has distilled over. R. H. Wisdom said that he had tested the matter and found that no appreciable error is introduced by differences in the degree of saturation of the xylol.

Mr. Reed asked whether the use of ether in saponification lowers the boiling point. Mr. Oberfell had no data on the actual boiling point when ether is added, but said that it must be high enough to give complete saponification, since the results for non-saponifiable agree closely with those obtained without ether. Mr. Reed suggested that oils which are difficult to saponify might not give concordant results when ether is used. Mr. Oberfell said he had found no reason to suppose so, and referred to the experience of workers in the oil laboratory of the Bureau of Chemistry, from whom he had got the idea. He further said that the use of the petroleum ether during saponification is merely a matter of covenience, to prevent bumping, and makes no difference to the results obtained.

Mr. Oberfell asked for opinions in regard to methods for total fat, whether this should be determined directly or by difference. T. A. Faust favored the difference method, believing that it gives more concordant results. Mr. Reed suggested that in

* At the *A. L. C. A.* Convention, Atlantic City, Dec. 5, 1913.

Digitized by Google

cases where the total fat was wanted, but not all the other things, it would be a saving of time to do it directly. Mr. Oberfell replied that since it is necessary to know the amount of unsaponifiable in order to subtract it from the sum of the fatty acids and unsaponifiable, there must be two determinations anyhow, and since the three things that must be determined in order to get the total fat by difference can all be determined with great accuracy, the difference method really gives better concordance than the other. W. H. Teas suggested that if the oil in question had been neutralized by ammonia, the fat determined by difference would be too high, since the ammonia would not be a part of the ash. Mr. Oberfell said that no provision for determining ammonia had been made, and admitted that if oils so neutralized were to be dealt with, the direct determination would be best. In this opinion Mr. Reed concurred.

Mr. Oberfell asked for opinions on methods for determining unaltered oil in sulphonated oils, but no one responded.

DISCUSSION OF COMMITTEE REPORT ON COLOR TESTS.*

In the absence of J. M. Seltzer, Chairman of this Committee, the report, which had been printed in the December JOURNAL, was presented by F. H. Small. The color tests made by the collaborators were exhibited.

R. W. Griffith inquired whether incompletely tanned skivers were found to be darker than those completely tanned. Mr. Small replied that they were. The precise method of tannage is immaterial, so long as it is complete. Mr. Griffith inquired whether a stronger solution should not be prescribed for finishing the skiver. Mr. Small replied that a 3 per cent. solution gives as strong a color as one having 5 or more per cent. L. Balderston mentioned that a color test made with a 90° barkometer liquor was almost identical in color with one made from the same liquor at the ordinary strength.

C. R. Oberfell inquired about the possibility of getting a supply of cow grain splits. Mr. Small replied that any tanner who has a splitting machine and a competent operator could furnish them.

* At the *A. L. C. A.* Convention, Atlantic City, Dec. 5, 1913.

Digitized by Google

Many hides must be sorted over to obtain a few that are suitable, since they must be free from blemishes. C. W. Norris asked about prices. Mr. Small said that $7 for a piece from 3 to 5 feet long and from 1½ to 2 feet wide, which is practically half a bend, is a customary price, and that nothing could be guaranteed even at this figure.

S. Saxe asked whether sheep skins from South America, Australia and France would give similar or different results. Mr. Small replied that he bought his sheep skins in the open market and did not know where they came from, but that they gave pretty concordant results.

T. A. Faust said that he had been getting sheep skivers specially prepared, and had been surprised at the poor results often shown. Mr. Faust described his method of handling the sheep skivers as follows: Place the skins in a borax solution, and at the same time start a rather mild bran drench. After one day, take them out of the borax, and without washing put into the drench. The skins are plump when they go into the drench, but in a day or two they fall. They are in good condition to use after about two days in the drench. If they are taken out of the drench and put into water they plump up, but by keeping them in a very low bran drench, using a handful of bran to a skin, they may be kept for a week or ten days in a suitably soft condition. These skins give good colors, rather dark, but nearly the color that the material will give in actual tannage.

Mr. Small said that his reason for preferring the boro-phenol method to one involving the use of a drench is that the latter involves a certain amount of skill and experience to handle the skins properly. In his own experience in the committee work, one skin was thin, and gave good results. The thicker one gave very poor results. It is practically impossible to lay down rules for the use of a bran drench, since judgment is a necessary factor in its success. For the boro-phenol process, on the contrary, it is possible to outline a procedure which can be followed in practically all cases.

Mr. Oberfell asked if he was correct in supposing that the bran drench is used to neutralize the borax or other alkali which has been used to draw the pickle from pickled skins, while the

Digitized by Google

boro-phenol is merely a preservative after the skin has been depickled and is ready to tan. Mr. Small replied that since the boro-phenol is slightly acid it may be used to first delime and then preserve limed skins, while if the skins are pickled, they must first be treated with alkali, and then the boro-phenol neutralizes the excess of alkali. A simple way is to use a weak organic acid to bring the skins to a condition practically neutral, and then rinse them and place them in the boro-phenol. The bran drench may be used, but he thought it preferable to use a weak solution of an organic acid for neutralization, then rinse out the small amount of salts formed and put into boro-phenol for preservation. A skiver left for a considerable time in a bran drench is likely to be strongly acid when it goes into the tanning solution, and Mr. Small thought that a color set in a strongly acid skin could hardly be a satisfactory color test. The degree of acidity affects the color.

Mr. Faust asked whether the method proposed by Mr. Loud in the JOURNAL (Feb., 1911, pp. 50-51) had been tested. The skins are put into a dilute solution of acetic acid. It gives rather light colored results, but consistent. Mr. Faust thought this method worth further trial. Mr. Small asked why, if the boro-phenol method is satisfactory, any other should be desired. Mr. Reed expressed doubt of the boro-phenol method being entirely satisfactory. Mr. Reed uses sheepskin skivers, and has always had trouble with them. He washed them in borax, neutralized the borax with acid, and laid them away in boro-phenol. Recently he has discarded the boro-phenol and substituted a saturated solution of common salt, from which the pieces are washed when needed. These skins give more uniform results than those preserved in boro-phenol. Mr. Small admitted that if low grade carbolic acid, containing iron, etc., were used, trouble might result, but he remarked that the best answer to Mr. Reed was the display of color tests made with skins prepared with boro-phenol which lay on the table. In answer to a question he further said that a 24-hour washing to remove the boro-phenol seemed necessary to insure good results.

Mr. Alsop asked Mr. Small whether, in his opinion, this year's committee work would justify the Association in adopting a pro-

Digitized by Google

visional method based on the use of skin. Mr. Small replied that the method outlined in the recommendations of the report comes nearer to being satisfactory than any he knew of, but that he could not give a confident answer, as he had not studied the set of tests shown with sufficient care.

Mr. Griffith suggested that if a plan were adopted which involved using skins which had been limed, and then put through a definite process of deliming and preserving, more uniform results might be obtained. He thought that much of the trouble which has been encountered is due to salts not thoroughly washed out, which react with the tannin to give products which affect the color. Mr. Dickerson agreed with Mr. Griffith that in order to secure comparative results the skins used should be put through the same treatment from the very beginning.

Mr. Kerr, in answer to a question, said that he had long ago given up hope of securing comparable results with skins. Mr. Reed said that the talk about getting colors like those which the tanner would get is futile, because it is not possible to be sure that the same material will give the same color on any two skins. Mr. Alsop remarked that one cause of disagreement on color tests is the fact that extract makers want light results, and tanners want dark ones. Mr. Kerr said he believed that while in any one laboratory good results might be obtained with skin tests, it was useless to expect concordance among different laboratories.

DISCUSSION ON SULPHITE-CELLULOSE EXTRACTS.*

Mr. Saxe introduced the subject by reading some correspondence which he had with Professor Procter.

107 Manhattan Ave.,
New York City, N. Y.
July 30, 1913.

PROFESSOR HENRY R. PROCTER,
% Leeds University,
Leeds, England.

DEAR SIR:—

Will you kindly give me the method which you use or recommend for the analysis of tanning extracts, and the exact wording

* At the *A. L. C. A.* Convention, Atlantic City, Dec. 5, 1913.

Digitized by Google

of the analysis? I am particularly interested in knowing whether you report tannin as tannin, as the Americans do, or whether you report it as matter absorbed by hide substance.

This prompts me further to ask what method you advocate for the analysis of Sulphite-Cellulose Extracts, and what per cent. or how many grams of hide powder you recommend, also whether you report it the same as tannins or whether you report it as matter absorbed by hide substance.

I am an associate member of the American Leather Chemists' Association and am interested in tanning extracts, but am not acquainted with the English method of reporting tanning materials,—hence this inquiry. In conclusion, would like to ask whether any exception could be taken if leather chemists reported Sulphite-Cellulose Extracts with the words "matter absorbed by hide substance" instead of the word "tannin."

Thanking you in advance for your kindness and consideration, I remain

Yours very respectfully,

SIGMOND SAXE.

Professor Procter replied, enclosing a copy of the form of report used at his laboratory, in which they do not use the word "tannin," but the expression "tanning matters absorbed by hide." In answer to the other questions, he referred to the Leather Chemists Pocket Book, in which the methods of the I. A. L. T. C. are given.

Mr. Saxe asked whether the tanning matter of sulphite-cellulose extract is to be reported as tannin or as matter absorbed by hide. R. W. Griffith read section 13 of the methods of the Association, "The tannin content is shown by the difference between the soluble solids and the corrected non-tannins, and represents the matters absorbable by hide under the conditions of the prescribed method."

H. H. Hurt said that he had just finished some leather tanned in sulphite-cellulose material alone, and the resulting leather is so good he thinks the tanning matters of sulphite-cellulose extracts ought to be called tannin.

W. H. Dickerson reported that a sample of leather tanned in

Digitized by Google

these liquors alone was analyzed by the official method. The water-extractive material was examined with minute care, and found to answer the tests for true tannin, and no evidence of any tanning matter other than true tannin could be found.

Mr. Hurt stated that the amount of water-soluble matter in leather tanned with sulphite-cellulose is less than in that made with vegetable tannins.

Another member mentioned the "syntans," and asked what should be done in reporting analyses of liquors containing these materials. He recommended that the use of the word "tannin" in reporting the results of analyses be discontinued, and that the word be replaced, as in the Leeds form, by the expression "matter absorbed by hide."

F. P. Veitch said that an invitation had been outstanding for some time for any one interested in sulphite-cellulose extracts to give a demonstration at the Leather and Paper Laboratory of the ability of these extracts to make satisfactory leather, but that the invitation had not been accepted as yet.

J. S. Robeson remarked that one reason for the low esteem in which these materials are held in many quarters is the fact that in some instances untreated waste liquors have been used, and of course these could only give poor results.

Mr. Saxe showed a piece of leather made with sulphite-cellulose liquor alone in 29 days, and said that it was a very good piece of leather. This was made by an oak tanner on his own motion.

Mr. Dickerson referred to some results published a year ago, showing that the water-soluble material in leather tanned with a mixture of sulphite-cellulose and quebracho was exceptionally low.

A motion was made that the Council be instructed to meet and take further action in regard to reporting sulphite-cellulose materials and report to the convention before adjournment. This motion was ruled out of order.

F. H. Small called attention to the acknowledged fact that the Association had no duty in regard to determining the tanning value of sulphite-cellulose extracts. The Association can only frame methods of analysis and direct forms of reporting the re-

Digitized by Google

sults of analyses. In defining tannin as material absorbable by hide, we have gone as far as we can, with our present knowledge. Until somebody finds a really satisfactory way of analyzing these materials, the best that we can do is to use the same method that is employed for vegetable tannins and report the matter absorbed by hide, whether under the name of tannin or not.

DETERMINATION OF PENTOSE IN TANNING MATERIALS AND EXTRACTS.*

By J. L. van Gijn and H. van der Waerden.

[These experiments were carried out in the Royal Experiment Station for the leather industry at Waalwyk, Holland, and published by the Department of Agriculture, Labor and Commerce, as Bulletin No. 6, 1913.]

Pentoses and pentosans are very common among plants and probably occur as the products of decomposition of hexoses under the influence of living cells. As is known the above compounds give furfurol when distilled with weak acids. But Tollens, de Chalmot, Cross and Bevans and others have found other compounds besides pentoses in plants, which also yield furfurol when distilled with weak acid.

Several determinations of pentosans in tanning materials have been published.

Investigator	Material	Pentose content per cent.
Tollens and Flint[1]	Oak wood	17.61
Councler[2]	Heartwood oak	18.44
Michelet and Sebelien[3]	Oak splint	17.33
	Oak bark	11.56-14.9
	Fir bark	10.32-11.0
	Oak wood†	19.06
	Oak bark (18 years)†	14.21
	Young oak bark†	12.88
Jedlicka[4]	Oakwood extract	4.3 - 5.3

The determination of pentoses as well as pentosans is best

* *Collegium*, Dec. 1913, pp. 639-645. Translated for the JOURNAL.

† Based on dry material.

Digitized by Google

made according to the distillation method of Tollens[5] and his associates, by which these compounds are transposed into furfurol, by boiling with 12 per cent. HCl, according to the following equation:

$$\text{Pentose } C_5H_{10}O_5 = C_5H_4O_2 + 3H_2O$$
$$\text{Pentosan } C_5H_8O_4 = C_5H_4O_2 + 2H_2O$$

The furfurol is next precipitated according to Councler,[2] by means of phloroglucin dissolved in 12 per cent. HCl, and the resulting black furfurol-phloroglucid is weighed.

$$\underset{\text{Furfurol}}{C_5H_4O_2} + \underset{\text{Phloroglucin}}{C_6H_6O_3} = C_{11}H_8O_3 + 2H_2O.$$

If methylpentoses or methylpentosans are present as well as pentoses, they are transposed into methylfurfurol by the HCl distillation, and this further condenses into methylfurfurol-phloroglucid when treated with phloroglucid (Vertocek[6]).

The methyl compound is red instead of black, and is soluble in 96 per cent. alcohol at 60° C. Vertocek[6] and later Tollens and Ellet[7] have made a detailed study of this condensation. Although the operation is less simple than with furfurol, a separation of the two substances may be brought about by extracting both phloroglucids from the weighed total precipitate by means of alcohol. This makes it possible to calculate the content of pentoses as well as methylpentoses from tables and formulae. (See also Kröben.[8])

Table I contains results from various tanning materials.

In comparing the results we were struck with the fact that quebracho extract was almost free from pentoses and pentosans and contained no methylpentoses, while in mangrove extract only rather large quantities of methylpentoses were found. This interesting fact caused us to investigate further to see whether by means based on this fact mangrove extract could be detected in quebracho extract. First we determined the content of these substances in guaranteed pure mangrove and quebracho extracts. The results of this investigation appear in Table II and served to corroborate the previous ones. Even with this guaranteed pure quebracho extract the amount of pentoses and methylpentoses is entirely different from that found in mangrove extract.

Digitized by Google

TABLE I.

Material	Grams weighed out	Cc. of distillate used	Mg. phloroglucid			Pentoses per cent.	Methyl pentoses per cent.	Total
			Furfurol	Methylfurfurol	Total			
Oak bark	2.0	200	123.0	2.0	—	16.2	—	—
"Garouille"	2.5	100	54.5	17.0	—	12.1	5.4	—
"Garouille"	2.5	100	57.5	25.0	—	12.6	8.2	—
Mimosa bark	2.5	100	21.0	1.0	—	5.3	trace	—
Mimosa bark	2.5	200	34.0	none	—	3.95	none	—
Quebracho wood	2.0	200	106.5	1.0	—	14.1	—	—
Mangrove bark	5.0	100	47.0	18.0	—	5.3	3.0	—
Myrobalans	2.5	100	—	—	60.5	—	—	13.2
Myrobalans	2.5	100	—	—	17.5	—	—	5.7
Valonia	2.5	100	68.0	3.0	—	14.8	trace	—
Divi-divi	2.5	100	26.0	none	—	6.4	trace	—
Guara	2.5	100	14.0	none	—	3.9	trace	—
Liquid oakwood extract	5.0	100	—	—	47.0	—	—	5.2
Liquid oakwood extract	5.0	100	—	—	68.5	—	—	7.4
Liquid oakwood extract	5.0	100	—	—	47.0	—	—	5.2
Liquid chestnut extract	5.0	100	—	—	45.5	—	—	5.1
Liquid chestnut extract	5.0	100	—	—	47.0	—	—	5.2
Liquid chestnut extract	5.0	100	—	—	52.5	—	—	5.8
"Garouille" extract	10.0	100	none	57.0	—	none	4.8	—
"Garouille" extract	10.0	100	none	52.0	—	none	4.3	—
Mimosa extract	10.0	100	—	—	none	—	—	none
Mimosa extract	10.0	100	—	—	none	—	—	none
Liquid "mimosa D" extract	5.0	200	—	—	none	—	—	none
Liquid quebracho extract	5.0	100	—	—	4.0	—	—	trace
Liquid quebracho extract	5.0	100	—	—	5.0	—	—	trace
Liquid quebracho extract	5.0	100	—	—	none	—	—	none
Liquid mangrove extract	5.0	100	none	26.0	—	none	4.3	—
Liquid mangrove extract	5.0	100	0.8	46.4	—	none	7.7	—
Liquid mangrove extract	5.53	200	1.0	54.0	—	none	4.0	—
Myrobalan extract	10.0	200	—	—	20.0	—	—	0.6
Myrobalan extract	10.0	200	—	—	25.0	—	—	0.8
Valonia extract	10.0	100	13.3	0.7	—	0.94	none	—
Divi-divi	10.0	100	15.0	2.0	—	1.1	0.65	—
Guara extract	10.0	100	16.0	1.0	—	1.1	none	—
Sulphite-cellulose	5.0	100	—	—	7.0	—	—	1.8
Sulphite-cellulose	5.0	100	—	—	25.0	—	—	3.1
Sulphite-cellulose	5.0	100	—	—	30.0	—	—	3.6

Digitized by Google

TABLE II.

Material	Weight in grams	Cc. of distillate used	Milligrams of phloroglucid: Furfurol	Milligrams of phloroglucid: Methyl-furfurol
1. Quebracho extract—"Pure Havre" liquid..	11.45	100	Traces	—
2. Quebracho extract—"Bisulphited" liquid..	7.55	100	Traces	—
3. Quebracho extract—"Lepetit" liquid.....	6.91	100	Traces	—
4. Quebracho extract—"Renner extract" liquid	6.2	100	Traces	—
5. Quebracho extract—"Argentine"(sulphited) solid.....	10.0	100	Traces	—
6. Mangrove extract—"Lepetit" liquid.....	5.25	200	Absent	32

Next various mixtures of quebracho and mangrove extract were prepared and these mixtures of known content examined in the same way. With untreated quebracho extract we were able clearly to detect as little as 10 per cent. mangrove extract (Table III), but with sulphited quebracho extract we could not detect less than 25 per cent. (Table IV).

TABLE III.—UNSULPHITED QUEBRACHO MIXED WITH MANGROVE.

Mixture	Percentage	Materials (liquid extracts)	Grams weighed out	Cc. of distillate used	Mg. phloroglucid: Furfurol	Mg. phloroglucid: Methyl-furfurol
1 ..	19.0..	Havre quebracho...	1.16	..250	1.0	42.0
	81.0..	Lepetit mangrove ..	5.00			
2 ..	32.0..	Havre quebracho...	2.42	..250	1.0	33.0
	68.0..	Lepetit mangrove ..	5.00			
3 ..	47.5..	Havre quebracho...	3.00	..250	1.0	18.0
	52.5..	Lepetit mangrove ..	3.32			
4 ..	62.0..	Havre quebracho...	5.30	..250	1.0	18.0
	38.0..	Lepetit mangrove ..	3.20			
5 ..	71.0..	Havre quebracho...	7.61	..all	5.0	29.0
	29.0..	Lepetit mangrove ..	3.12			
6 ..	77.0..	Havre quebracho...	10.17	..all	7.0	31.5
	23.0..	Lepetit mangrove ..	3.33			
7 ..	83.0..	Havre quebracho...	15.40	..all	17.0	22.0
	17.0..	Lepetit mangrove ..	3.11			
8 ..	85.8..	Havre quebracho...	20.80	..all	21.0	23.0
	14.2..	Lepetit mangrove ..	3.45			
9 ..	90.0..	Havre quebracho...	16.30	..all	14.0	18.0
	10.0..	Sulphited mangrove	1.80			
10 ..	90.0..	Renner quebracho..	18.20	..all	2.0	15.0
	10.0..	Sulphited mangrove	2.005			

Digitized by Google

TABLE IV. –SULPHITED QUEBRACHO MIXED WITH MANGROVE.

Mixture	Percentage	Materials (liquid extracts)	Grams weighed out	Cc. of distillate used	Mg. phloroglucid: Furfurol	Mg. phloroglucid: Methylfurfurol
1	95	Havre bisulphited quebracho	5.010	200	none	none
	5	Sulphited mangrove	0.265			
2	90	Havre bisulphited quebracho	5.020	200	none	none
	10	Sulphited mangrove	0.500			
3	80	Havre bisulphited quebracho	4.010	200	2.0	2.5
	20	Sulphited mangrove	1.000			
4	70	Havre bisulphited quebracho	3.510	200	1.0	10.0
	30	Sulphited mangrove	1.560			
5	17	Havre bisulphited quebracho	1.010	250	1.0	37.0
	83	Lepetit mangrove	5.000			
6	32	Havre bisulphited quebracho	2.400	250	—	29.0
	68	Lepetit mangrove	5.030			
7	75	Havre bisulphited quebracho	9.200	all	1.5	3.5
	25	Lepetit mangrove	3.100			

In our opinion the fact that the formation of methylfurfurol does not take place readily under those conditions must be attributed to the influence of the bisulphite treatment, although a sulphited mangrove extract gave good results. We have, however, found that by adding enough iodine to combine with the free sulphurous acid this hindering action may be stopped. So if one has a sulphited quebracho extract before the HCl distillation is begun it must be treated with iodine and heated about 15 minutes with a reflux condenser, in order to oxidize the SO_2. If there is excess iodine in the distillate it will not influence the furfurol condensation (Table V).

It often happens that a quebracho extract mixed with mangrove also has some myrobalan extract in it to give a better color. This can of course be detected by other means, but it is of interest to us to see whether this admixture has any influence on our method. Table V clearly shows that it does not.

If one suspects less than 10 per cent. of mangrove extract, still the color change in the operation will be characteristic and it will pay to subject a larger quantity of the sample to distillation. We believe that we may positively state that mangrove extract may be detected in quebracho extract by this method, which we

Digitized by Google

recommend to our colleagues for trial. In conclusion we propose the following method of work.

Place 10 g. of the sample with a few glass beads into a tubulated retort in which some paraffin has previously been melted in order to guard against foaming. If the extract is sulphited it must be gently heated 15 minutes on a reflux condenser with enough iodine to combine with all the SO_2 and 100 cc. of 12 per cent. HCl. Otherwise only the HCl is added. The retort is then connected with a condenser and heated in an oil bath of 145° C. or over a free flame. After 10 minutes 30 cc. of 12 per cent. HCl is added through a funnel for each 30 cc. of distillate which has passed over. The distilling is continued until a drop of the distillate shows only slight rose color with anilin-acetate. Usually 420 cc. of distillate is enough, for further distilling is pointless and does not influence the results. Next bottle known volumes, filter the loose paraffin out, and add to the aliquot part of the filtrate an excess (200 mg. is enough) of phloroglucin dissolved in 12 per cent. HCl. Let the precipitate stand 15 to 24 hours, and filter through a weighed Gooch crucible with an asbestos mat, wash it free from HCl, and dry in a water oven at 98°-99° C. for 3 hours. The increase in weight is the sum of the phloroglucid of the methyl-furfurol and the furfurol. The precipitate is now treated with 30 cc. of 96 per cent. alcohol, washed with 50 cc. alcohol, dried at 98°-99° C. and weighed again. The loss in weight is the methyl-furfurol-phloroglucid.

In Tables II to V the values have not been transposed into pentose and methylpentose, as the figures given do just as well in the cases in hand.

We wish to remark further, that the color change following the addition of phloroglucin to the liquid is very characteristic and shows plainly whether the quebracho extract in question is pure or not. In the first case the liquid becomes yellow, then green, and gradually more or less black precipitate forms, while the liquid is left colorless. The distillate of a mangrove extract gives first a yellow color which then changes into red, while a red precipitate forms which turns brownish as it stands. In mixtures transition colors are formed which are very different from the above and prove the presence of mangrove extract.

Digitized by Google

TABLE V.—SULPHITED QUEBRACHO EXTRACT IN MIXTURES WITH MANGROVE AND MYROBALANS. THE QUEBRACHO USED IS NO. 26 OF TABLE I, AND THE MYROBALANS NO. 30 OF TABLE I. EXCEPTING MIXTURES 3 AND 5, 8 CC. OF N/10 IODINE WAS ADDED IN EACH CASE. ALL THE DISTILLATE WAS USED IN EACH CASE.

Mixture	Percentage	Materials	Grams weighed out	Mg. phloroglucid: Furfurol	Mg. phloroglucid: Methylfurfurol
1	100	Quebracho	20.5	trace	trace
2	82	Quebracho	20.7	2.5	17.5
	18	Sulphited mangrove	4.65		
3	83	Quebracho	20.4	1.5	16.5
	17	Sulphited mangrove	4.07		
		(50 cc. iodine)			
4	82	Quebracho	10.5	11.0	9.0
	18	Myrobalan	2.0		
5	84	Quebracho	10.1	10.5	5.0
	16	Myrobalan	2.0		
		(No iodine)			
6	94	Quebracho	13.2	4.0	0.0
	6	Myrobalan	0.8		
7	67	Quebracho	10.0	20.5	59.5
	20	Sulphited mangrove	3.0		
	13	Myrobalan	2.0		
8	83	Quebracho	12.5	4.5	20.0
	10	Sulphited mangrove	1.5		
	7	Myrobalan	1.0		
9	88	Quebracho	13.2	4.0	8.0
	7	Sulphited mangrove	1.0		
	5	Myrobalan	0.8		

BIBLIOGRAPY.

1. *Berichte der Deutschen Chem. Gesellschaft*, 1892 (25), p. 2912.
2. *Chemiker Zeitung*, 1894 (18), p. 966.
3. *Chemiker Zeitung*, 1906 (30), pp. 357-401.
4. *Collegium*, 1909, p. 126.

5a. *Zeitschrift f. angew. Chemie*, 1896, pp. 37-40.

5b. *Berichte d. D. Chem. gesellschaft*, 1905, p. 492.

6. *Berichte d. D. Chem. gesellschaft*, 1897, p. 1195 (30).
7. See 5a.
8. *Journal für Landwirtschaft*, 1900 (48), pp. 357-384.

Digitized by Google

ABSTRACTS.

Leather and Fur Trade at Nizhni Novgorod Fair. VICE-CONSUL GENERAL ALFRED W. SMITH, Moscow, in *Daily Consular and Trade Reports.* The Trade in leather and rawhides at the Nizhni Novgorod fair (which lasted from July into September) this year was satisfactory to both manufacturers and dealers. The aggregate of sales was fully up to that of 1912 and high prices were easily obtained. In some varieties, such as sole leather, the supplies were insufficient for the demand. The market continued firm throughout the fair, interest flagging only toward the end, after the demands of the interior market had been satisfied, and the termination of the Balkan war brought a diminution in the Near Eastern demand. Prices weakened in the closing days of the fair.

The manner in which payments were made at this year's fair was very satisfactory. A considerable amount of goods were sold for cash, which indicates that conditions on the Russian market are becoming more satisfactory, and prospects for the immediate future at least are better. The trade in hides was brisk and cash payments increased. All kinds of hides were disposed of at prices considerably above those of last year. These high prices held trade back at the opening of the fair. Foreign buyers held off, urging a fall in prices, and the campaign was opened by Russian manufacturers, who purchased hides in small lots in spite of the high prices, as the trade in dressed leather had been satisfactory and the supply of rawhides at the different factories had become greatly reduced. Seeing that the anticipated fall in prices was not forthcoming, foreign customers began buying about August 10, and in about two weeks nearly the entire supply was sold.

The supply of yalovka (heifer hides) amounted to about 350,000 pieces and was disposed of principally in the interior market. Large-size Siberian and local Russian yalovka, weighing 15 to 18 pounds avoirdupois sold for $28.52 to $29.23 per 100 pounds at the beginning of the fair, and for $26.38 to $27.81 per 100 pounds at the close. Small-size yalovka, weighing 6 to 12 pounds, brought $25.67 to $29.95 per 100 pounds. The better grades were disposed of at the height of the season, so that the lower prices at the close were for lower grades.

The supply of oxhides was small, about 80,000 pieces, and was entirely disposed of in Russia. Hides weighing 22 to 26 pounds avoirdupois sold at $25.67 to $26.38 per 100 pounds. The entire supply of slaughtered calf hides, 72,000,000 pounds, was sold to foreign purchasers in three or four days, at $45.63 to $49.91 per 100 pounds. No business was done at the opening of the fair, as traders had bought at high prices, while foreign buyers had come prepared to buy at $40 per 100 pounds. Not a single transaction was concluded at that price, however. The supply of diseased calfskins amounted to 36,000,000 pounds and brought $31.37 to $34.22 per 100 pounds. About 25,300,000 pounds remained at the close of the sale, which foreigners seemed inclined to buy at $28.52 per 100 pounds, but $32.80 was demanded. Velikoustiug and Vologda calfskins

Digitized by Google

were represented at the fair by samples and sold at $50.62 and $48.84 per 100 pounds, respectively.

There was a fair demand for horsehides, and the goods were taken by the domestic and foreign markets, in about equal quantities. The total supply was about 800,000 hides. A shipment of about 300,000 hides was sold before the beginning of the fair for exportation to America. The prices during the fair ranged as follows: Russian heavy, 20 to 22 pounds, $3.60 to $3.73 per piece; Siberian heavy, 18 to 19 pounds, $3.14 to $3.16 per piece; Guryev, $2.97 per piece. There was only a limited demand for foal hides, colored being offered at $1.28, as compared with former prices of $2.57 to $3.09 per piece, but purchasers were not willing to pay more than $0.97 to $1.03. Siberian was offered at $0.77 per piece.

The entire stock of approximately 1,000,000 sheepskins was sold to foreigners at very high prices, the bulk going to Germany. America took about 200,000 pieces. The prices were as follows: Belebeyev, $0.69 to $0.72 per piece; Menzelin, $0.66; Kazan, $0.61 to $0.66; Viatka, $0.59 to $0.64. The supply of goatskins was not large and not much business was done in that branch. Bogorodsk manufacturers took the supply of camel hides (about 200,000 pieces) at $13.55 to $17.11 per 100 pounds. In general, prices of yalovka, oxhides, and horsehides showed an increase of 15 to 20 per cent.; sheepskins, a gain of 20 to 25 per cent., and calfskins a decrease of 10 to 15 per cent.

Cutch. CHAS. EACHUS, in *Hide and Leather*, Jan. 3, 1914. The solid tanning extract known as cutch is made from the bark of a special variety of mangrove tree that grows in Borneo. The original material known as cutch was a solid extract made in India from the wood of the acacia catechu, and it was used extensively for dyeing. This dyeing cutch is hard to dissolve in water, giving a dirty brown color on leather. Some other mangrove cutches have been made chiefly to replace the real acacia cutch in dyeing, but they have not found any use in the leather industry on account of the dark red color. At the present time the true tanning cutch is made of the tengah bark, or bastard mangrove that grows in Borneo. This bark is much lighter in color than other mangrove barks, and the tannin infusion made from it is also lighter colored.

The mangrove trees follow the equator around the world. There are many different species of mangrove, and this has led to different opinions of the bark as a tanning material, because different chemists had different kinds of mangrove to work with. Some mangrove tannins are much more astringent than others, combining with hide substance more firmly. In equatorial South America, Florida, Australia and the Philippines the inferior varieties of mangrove are found; the percentage of tannin in the bark being low, and the tannin can sometimes be washed out of the hide after tanning.

In Borneo, Madagascar and Zanzibar the best mangrove bark for high percentage of astringent tannin is found. The Borneo bark is the only mangrove bark known to commerce at the present time which will give

Digitized by Google

the light, golden color on leather. This is chiefly due to the variety of mangrove, and to careful stripping of the bark and up-to-date methods of making the extract.

In Borneo there are extract plants making this mangrove cutch by the same process employed in making solid ordinary quebracho, but it is not chemically treated like most quebracho. During the litigation a few years ago in regard to letting cutch into this country free of duty it was proven that Borneo cutch was not chemically treated, and that the excellent light color is due to the bark naturally, some of the bark having been placed on exhibition.

The mangrove barks from outside of Borneo are so red and the tanning extracts therefrom are so red and oxidizable that they can be used only for helping out hemlock tannages. The Borneo cutch, on account of its fine color, can be used in making any class of vegetable tanned leather. It blends well with hemlock, oak and all other well known tanning materials, for the tanning of heavy as well as light leathers, and one very great advantage in using cutch lies in the fact that it contains very little insoluble matter, consequently gives very little sediment in contrast with ordinary quebracho, which contains from five to six times as much as cutch in the original analysis, but which may contain twenty times as much insoluble in a strong tan liquor.

The following table, taken from a foreign leather trade journal, gives the results of some experiments with various tanning materials, showing how much sediment is deposited by each in a liquor of 14° barkometer after sixty days' standing. This formation of sediment is proportional to the transformation of soluble into insoluble tannins:

	Per cent.
Cutch	0
Gambier	0
Mimosa bark	2
Quebracho	4
Oak bark	7
Pine bark	10
Chestnut wood	11
Myrobalans	26
Valonia	26
Divi divi	29

It is to be noticed that there was no change in the liquor made from cutch, and which blended with any tanning material causes no precipitation or loss of tannin.

The average analysis of cutch is as follows:

Digitized by Google

	Per cent.
Moisture	19.84
Total solids	80.16
Soluble solids	79.10
Insolubles	1.06
Non-tannins	20.94
Tannins	58.16

This shows an extract with 5 per cent. more solids than solid quebracho and only 1 per cent. of insolubles. For making an extract to drum into sole leather this high percentage of solids is important.

Cutch is recommended to replace hemlock, oak and quebracho, and when used with quebracho helps to reduce the insolubles, which exist to such a large extent in quebracho liquors, and which are undesirable. It has been known for several years that cutch mixed with quebracho in a liquor helps to keep the insolubles of the quebracho from separating in the tan vats.

The Distinction between Bark Tans and Fruit or Wood Tans. B. KOHNSTEIN. Lecture before the Austrian Section of the I. A. L. T. C., Nov. 16, 1913. *Collegium*, 1913, pp. 645-648. Tannins may be divided into two, perhaps three classes, according to whether they contain tanning material which gives green or blue with iron or whether when heated with caustic potash the tannins change into protocatechu, *i. e.*, phloroglucol, or into acetic acid; or whether under the same conditions it gives gallic or ellagic acid. The first are called catechol, the second pyrogallol tannins. A division may also be made on the basis of coloring with vanadin salts. Catechol and pyrogallol tannins may also be distinguished by heating carefully to 160°-215° C. and seeing whether catechol tannin or gallic acid is produced (Procter, *Leather Industries Laboratory Book*, p. 50). These groups may also be distinguished by the diazo-benzol chloride method of Nierenstein which precipitates only the protocatechol tannins not the pyrogallol ones; or by Stiasny's method with formadehyde and HCl which also rests on precipitation of the protocatechol tannins. In any case exact distinctions are difficult.

In 1862 Stenhouse (*Dingl. poly. J.*, 1862, p. 150) found that all tannins which give blue black precipitates with iron salts contain sugar and hence may be called glucosides, while those which turn iron green yield no sugar with the exception of the willow tannins.

If we boil extract of fir or other conifers or of willow with HCl, cool it, shake it down with ether, take off the clear upper layer of ether, replace it with ammonia and shake, we have beautiful green solutions.

Not only conifers and willow barks extracted with alcohol and boiled with HCl give a green color with excess of ammonia which, however, disappears very quickly because it is usually hidden by the formation of phlobaphenes in the presence of HCl. If we boil a water extract of fir bark with HCl we obtain a brownish red precipitate $C_{42}H_{34}O_{17}$ which is purified by treatment with alcohol and ether.

Digitized by Google

Alcohol Extract of Tanning Materials.

30 grams, 10 per cent. tanning substance } To 1 liter alcohol
10 grams, 40 per cent. tanning substance }
5 cc. of this boiled with 2.5 cc. HCl.

Tanning material	Color of alcohol extract	Color after boiling with HCl	Color arising when the esterified solution is put on solid caustic potash	Color of the alcohol solution boiled with HCl and shaken with ether
Fir	Orange	Deep purple	Green	Green
Hemlock	Light red	Scarlet	Green	Green
Larch	Light red	Purplish red	Green	Green
Mangrove	Red	Dark red	Malachite green	Blue green
Willow	Bright yellow	Pink	Green	Green
Oak	Yellow	Red	Green	Green
Mimosa	Brownish yellow	Violet	Malachite green	Green
Kuoppern	Dirty yellow	Red	Green, becoming brown	Light green
Sumac	Yellowish green	Light pink	Green, becoming yellow	Leaf green
Quebracho wood	Blood red	Violet red	Olive	Brown
Myrobalan	Yellow	Yellow	Brownish yellow	Brownish yellow
Oak wood	Yellowish brown	Yellowish brown	Brown	Brown
Chestnut wood	Yellowish brown	Yellowish brown	Brown	Brown
Divi-divi	Yellow	Intense scarlet	Brown	Brown
Algarobilla	Yellow	Red	Yellowish brown	Brown
Bablah	Yellowish brown	Yellowish brown	Brown	Brown
Trillo	Yellow	Dark yellow	Olive	Brownish yellow

Digitized by Google

If we take alcohol extracts of tannins and boil these with concentrated HCl, or introduce well washed HCl gas into a solution of the tannin while heating it on a reflux condenser, most tannins form a deep red soluble compound like that of fir. When ammonia is added a green color would very seldom occur except with fir and willow. But the following method determines the color change exactly.

Place a piece of solid potassium hydrate on a white dish, moisten it with water and then drop on it one drop of the tanning solution which has been boiled with the alcohol and further heated with HCl to the boiling point. Often a splendid malachite green will appear which changes to brown in the air. Leaf and bark extracts give this green while fruit and wood (unless it contains bark) give a dark color immediately. There is another way of distinguishing tannins by color reaction.

Take about 5 cc. of an alcohol solution of the tannin and boil with 2.5 cc. concentrated HCl in a test-tube. Cool, shake with ether, add cold water to separate the ether, take it off and replace with ammonia. When shaken the ammonia solution becomes green, blue-green or brown.

The accompanying table gives various steps in the recognition of bark and leaf tannins in contrast to wood and fruit tannins.

The pathological tanning material, knoppern, also causes green color, and a weak olive brown color is shown with many young valonia acorns. Sumac leaves were examined which gave leaf green color when shaken up with ammonia after having been treated with ether.

E. A. B.

A Patent for the Preparation of Leather from Artificial Hide. W. EITNER. *Der Gerber,* Jan. 1, 1914. A German gas light company has taken out a patent with the above purpose. The artificial "hide" is composed of micro-organisms (bacteria and moulds) and resembles hide to a remarkable degree. A preliminary treatment before tannage is necessary to secure a smooth and pliable leather. Alkalies, such as caustic soda or sodium sulphide may be used. The "hide" is grown by inoculating a solution of beer-wort containing ½ per cent. of alcohol with certain micro-organisms and keeping the solution at a temperature of from 20 to 35° C. The growth covers the surface of the liquid to a considerable thickness. The leather made from this is about 1/20 as thick as the wet film. Since the "hide" may reach a thickness of a foot, it is possible to make a very thick leather (about 29 iron!). The micro-organisms may be grown about a fabric, or mixed with cork meal or other solid material.

The "hide" consists of cells imbedded in a mucus, secreted by the cells, having a constitution resembling sugar. Neither cells nor mucus have much inclination to unite with tannin. Hide is made up of interlaced fibers, which give it its strength. The chains of cells in the bacterial "hide" are not interlaced, and when the mucus is dissolved out by alkali they would simply fall apart unless held together by other fibrous material intermingled. Glue is added also before tannage, to help fix tannin. The

Digitized by Google

author does not anticipate that the new sort of "leather" will have any great vogue. L. B.

Sulphuric Acid in Leather. LOUIS SODY. *Gerber Courier*, 1913 (54), No. 37. So far there is no reliable method for distinguishing sulphuric acid originally present in the leather from that produced from other sulphur during the analysis. The Ballard and Maljean method is referred to, whereby total and free (volatile) sulphuric acid are determined. Some specifications set a limit only for total sulphuric acid; this is unjust to the producer, for only the free acid is harmful.

There are various sources of free sulphuric acid in leather. The natural sulphur of the hide can theoretically furnish 0.25-0.375 per cent. total sulphuric acid on analysis. In practice not all the natural sulphur is retained in the leather and these figures are high. The nature of the water used may often affect the sulphur content of the leather. Also the salt used in preserving hides often contains sulphates and these are not entirely removed in soaking. The sulphide used in liming is retained to some extent. To utilize the tannin in the spent bark of the pits, sulphites are used to bleach the color and make the residual tans more soluble. Some sulphur is sure to be retained in the leather. Tanning oil prepared by sulphonating castor oil may also introduce sulphuric acid.

W. J. K.

Determination of Free Sulphuric Acid in Leather. J. PAESSLER. *Ledertechn. Rundschau*, 1913 [5], 377. The usual quantitative process gives incorrect results when Neradol D has been used in the manufacture and requires modification in this case. A method is being worked out at the Freiberg Institute.

W. MOELLER, *Ibid*, p. 385—Criticizing the above as reflecting upon Neradol alone, the author asserts that the methods for this determination were open to reproach before Neradol was introduced. A method free from objection does not exist (see Sody, above) and it will be a welcome improvement if one is devised at Freiberg. W. J. K.

Tender Grain and Its Prevention. W. EITNER. *Gerber*, 1913 (39), 281-3, 295-7. Since upper leather is now made only from grain leather, there is more liability to defective grain since the inferior hides are no longer made into waxed leather. The preparation of the firm elastic grain required for upper leather is the affair of the tanner, and the currier cannot remedy the defects although he can ruin a properly tanned leather. One source of faulty grain lies in the soaks. Formerly when old liquors were used the decayed spots already present in the dried hide became greatly enlarged by fermentation. Although old soaks are no longer used, fresh water is not best in all cases. For hard imported hides intended for chrome kid, 1-2 per cent. of their weight of caustic soda is added; for glacé lambskins, 1 per cent. soda. The dried hides are first left a day in a used soak, and then 24-40 hours in a fresh,

Digitized by Google

sharpened soak. Sod. sulphide may be used (5 to 10 per cent.) for coarse hides, buffalo, horse and kips, also when the hair or wool is of less value. Acid also may be used in softening kips as proposed by Seymour-Jones (Abstr. this JOURNAL, 1912 [7], 336. The swelling is equal to that produced by sulphide and the hair is not injured. The principal advantage is the resulting of a superior grain. Oxalic and sulphuric acids are unsuited, giving precipitates in the limes. Formic acid is best and cheapest of the organic acids. To remove the swelling produced by the acid, a salt pickle is recommended; before liming the salt is washed out. The short liming process used in modern sole leather tannage has also been introduced in the manufacture of upper leather. Faults in grain arising from intensive liming are hereby avoided:

Two forms of defective grain are met with at the present time, one a breaking of an otherwise sound leather, the other a tender ("mürbe") grain which tears on stretching; in this case the entire leather is fragile Formerly tender grain was due to fermentation in old soaks or in lengthy liming; pure lime does not injure the grain even if prolonged. The modern process of quick liming (Zähäschern) may cause a weak grain not from the operation itself but through the vigorous mechanical cleansing afterwards necessary. The body of the leather is not sufficiently loosened and the grain slides over this in working and becomes puffy. Too long watering after liming was formerly a source of tender grain (through fermentation) but in these times the fault frequently originates during the deliming. If the acid used for this purpose be added too rapidly the grain becomes swollen and weakened. The acid should therefore not be added faster than neutralized as controlled by testing with litmus paper. A similar source of brittle grain is from the use of sour liquor from the bran bate for deliming, the usual process being to employ the bath directly in the same way as the sweet bran. It should be used diluted and re-strengthened as neutralized. The deliming is sufficient when a section shows but a slight reaction for lime with phenolphthalein or litmus in the center. It is better to fall short than over-acidify with damage to the grain. Imperfect cleansing in the beamhouse may cause fragile grain. If the scum is not removed, it combines with the tannin and produces brittleness. The albumens dissolved by the lime are again precipitated by acids firmly in the fiber, hence it is necessary to thoroughly cleanse before deliming. Brittle grain and even brittle leather may result from using bating baths too hot. For the puer baths, etc., 100° F. is the limit and 80° F. is enough for acids.

During tannage only the brittle type of defective grain is formed. It is often assumed to come from starting the tannage in too strong liquors, but such are used in modern methods without grain fracture. Too much acid in the vats is the principal cause of the evil which may then result even with liquors weak in tannin, the first symptom being a shrinkage of the grain. Where it is necessary that the white hide be plumped, the practice is to first protect the grain by tanning it in sweet liquors. Turbid liquors such as those prepared from Argentine extract choke the swollen

Digitized by Google

grain, resulting in brittleness. These are unsuited in general for the fore-tannage and should not be used for this. Finally leathers which after tannage contain unfixed tannin or other substances is prone to fragile grain. To prevent this so-called water soluble oils are applied. These are sulphonated fatty acids neutralized with ammonia and mixed with mineral oil. W. J. K.

Carnauba Wax. C. LÜDECKE. *Technikum*, 1913, 393-407. This wax obtained from the leaves of a palm cultivated in Brazil has been in the market about 50 years. The amount produced is limited and always in demand; market fluctuations depend only on the variations in harvest and the manipulations of speculators. The only adulterations met with are paraffin and rosin. These lower the melting point and make the wax somewhat softer. Lately the Mexican candelilla wax has been fraudulently substituted for or mixed in bulk with Carnauba wax. After gathering the wax is melted and the chilled mass, which is very hard, is broken up and comes into the market in various grades of color, light yellow to brown-black. The wax contains up to 8 per cent. of dirt; "Courant" gray wax, obtained by melting in water, is free from dirt but retains considerable water.

The melting point of the crude wax is 83-86° C. For its determination a thermometer with a spherical bulb has this coated with a film of the wax by dipping into a melt over the water-bath. A test-tube with cork is jacketed over the lower part of the thermometer as an air-bath and the whole heated in a beaker of water until the wax film melts and drops from the bulb. The specific gravity of the wax is 0.992; the adulterants which affect this, paraffin (sp. gr. 0.76-0.79), ceresin (0.83-0.92), are more exactly proven by determination of melting point and unsaponifiable.

The chemical constants are important in testing the purity. The saponification with the usual alcoholic potash is difficult and the following modification is used. The shaved wax (2-2.5 g.) is heated 10 minutes to complete solution with an accurately neutralized mixture of 30 cc. xylol or benzol with 20 cc. 96-98 per cent. alcohol (invert condenser) and then titrated with N/2 alcoholic KOH phenolphthalein, reheated and again titrated if necessary. Then 25 cc. more KOH are added, boiled one hour, 50 cc. neutral alcohol then added, again heated ¼ hour, titrated rapidly with N/2 HCl, adding more alcohol to clear turbidity if needed. The whole is again boiled ¼ hour and titrated if necessary to complete neutrality. The constants for the pure wax and adulterants are:

	Acid number	Saponification number
Carnauba wax	22- 36	60- 84
Candelilla wax	13- 18	50- 60
Rosin	146-180	168-195
Japan wax	19- 24	214-224
Stearic acid	195-200	195-200
Paraffin	0	0

Digitized by Google

Since Carnauba wax saponifies easier in presence of soap, the author to determine unsaponifiable, heats 5 g. wax with 2 g. pure (or of known content unsapon.) olein, 5 g. NaOH, 10 cc. H_2O, and 30 g. spirit 2-3 hours. The solution is then concentrated, 2 g. $HNaCO_3$ added and evaporated to dryness with 20 g. ignited sand. The residue is extracted with petrol. ether in a Soxhlet apparatus. If the dried extract exceeds 55 per cent. (= wax alcohols), the excess is reckoned as paraffin. Adulteration with rosin is indicated by the acid number; 5 per cent. raises it to 13-19. The test is confirmed by hot extraction with 70 per cent. alcohol which remains nearly wax free on cooling and contains only the rosin (also stearic acid if present). Montan and candelilla wax also raise the acid number, but rather (especially with candelilla wax) lower the saponification number. The iodine number and refractive index are not of use in detecting admixtures.

Carnauba wax is used to harden inferior waxes, a small addition having a disproportionally marked effect. With alkalies it saponifies with difficulty, yielding emulsions of soap and unsaponifiable wax alcohols, etc., which are used in preparing liquid wax soaps for shoe dressing, furniture polish, paper and textile industries. Different products result according as caustic or carbonated soda and potash are used. A partial saponification is employed for purifying the crude wax. The only substitute used for Carnauba is montan wax. A recent patent (D. R. P. 234,504) hardens wool fat as a substitute for waxes. W. J. K.

PATENTS.

Impregnating Solids and Liquids. British Patent No. 18,536. A. R. BULLOCK, Cleveland, Ohio. Solid or substantially solid substances are impregnated with a liquid or plastic mass of impregnating-substance by the action upon the substances of a magnetic field which changes density, preferably with great rapidity. The process is applicable, for example, in preserving or curing meat, hides, or other forms of animal or vegetable matter, and in the tanning of hides.

Decolorizing Tanning Extracts. British Patent No. 18,436. W. HILDT, Warsaw, Poland. 5 kg. of soda are stirred into 1,000 liters of mangrove extract of 21° Bé., and 5 to 6 kg. of stannous chloride are added, and the extract heated to 90° C. For a like quantity of quebracho, 8 kg. of soda and 4 to 5 kg. of stannous chloride are used.

Treatment of Skins. British Patent No. 19,239. L. A. GROTH, West Kensington. The skins are hung into a vat from cross bars supported by a frame. The frame is moved horizontally so that the skins travel edgewise back and forth through the liquor. The process is applicable to soaking, liming, pickling and tanning. Electric current may be passed through the skins as they hang in the liquor.

Digitized by Google

Leather Rolling Machine. U. S. Patents Nos. 1,080,943 and 1,089,479. H. W. WINTER, Methuen, Mass.

Tanning Material. U. S. Patent No. 1,080,970. MAX HÖNIG, Brünn, Austria-Hungary. A process for the manufacture of tanning material from sulphite-cellulose waste liquors. The liquor is treated with sulphuric acid in amount sufficient to decompose only a part of the compounds of calcium with lignin and sulphur, and then adding a soluble sulphate, to decompose the remainder.

Leather-Board. British Patent No. 14,527. W. P. THOMPSON, Liverpool. The materials used are shredded leather, cellulose, a mineral acid and sodium bichromate.

Vacuum Vessel for Tanning. British Patent No. 15,345. J. DENNISS AND W. L. Fidler, Sydney, Australia. The vessel is made of reinforced concrete and immersed in liquid contained in an outer vessel.

Arrangement of Vats for Tanning. British Patent No. 15,346. J. DURIO, London.

Method of Treating Quebracho. U. S. Patent No. 1,081,730. J. M. Fiske, New York. Solid extract is treated with warm water and allowed to settle The liquid is then drawn off to separate it from the reds.

Leather Working Machine. U. S. Patent No 1,077,207. F. WAYLAND, Salem, Mass.

Process of Disinfecting Hides and Skins. U. S. Patent No. 1,083,300. OTTO RÖHM, Darmstadt, Germany. The hides are treated with a solution of a copper salt from which the copper is not precipitated by alkalies, added to a strong solution of common salt.

Hide-Working Machine. British Patent No. 20,002. M. H. SMITH, London.

Process of Depilating Hides and Skins. U. S. Patent No. 1,082,911. OTTO RÖHM, Damstadt, Germany. The unhairing is brought about by the action of a tryptic enzym. This method was outlined in an abstract on p. 408, 1913.

Extraction Apparatus. U. S. Patent No. 1,082,304. H. J. CARY-CURR, Chicago, assignor to E. H. Sargent Co. A scheme of arrangement of Soxhlets in a circular series.

Leather Seasoning Machine. U. S. Patent No. 1,082,244. CHARLES E. SLOCOMB, Wilmington, Del.

Treating Sulphite-Cellulose Lyes. British Patent No. 19,600. M. PLATSCH. Frankfurt a. M., Germany.

Leather-Dressing Composition. British Patent No. 20,554. A. VACHERON, Lyons, France. A mixture of pine oleo-resin, cod oil, petroleum and nitrobenzene.

Apparatus for Desiccating. U. S. Patent No. 1,082,468. L. C. MERRELL, Syracuse, N. Y.

Digitized by Google

Leather Manufacture. British Patent No. 14,248. P. CASTIAU, Renaix, Belgium. Hides are tanned partly with chrome and partly with vegetable tannin, and then rendered impervious by treatment with resins.

Machine for Working Leather. U. S. Patent No. 1,077,346. A. HODGES AND F. COOPER, Yeovil, England.

Water-Proofing Chrome Leather. British Patent No. 17,228. I. Winther, Roskilde, Denmark. The waterproofing material is a mixture of sugar, Japan wax, rosin, turpentine, tallow and paraffin.

Sulphonated Fats, Waxes, Etc. British Patent No. 18,333. I. LEVINSTEIN, Manchester. Sulphonic acids of fats, waxes, etc., which have a substantial content of palmitic acid and are ordinarily in the solid or semi-solid condition, are produced by liquefying the fat, etc., and treating the liquefied substance with sulphuric acid. The sulphonic acids or their salts, which are miscible with hot water, when mixed with waxes and greases, such as Japan wax, beeswax, tallow, etc., give rise to compositions also miscible with water and suitable for use as finishes for textile fibers and materials. The sodium salt of sulphonated palm oil, when melted with lanoline, gives a composition suitable for pharmaceutical uses. A composition giving an emulsion in water may be made from the ammonium salt of sulphonated palm oil by melting the free acid with mineral wax and then adding ammonia until a slight alkaline reaction occurs. According to the Provisional Specifications, any oils, fats, waxes, etc., containing palmitic acid may be sulphonated, and the sulphonic acids and their salts used to render vegetable, animal, and mineral oils, waxes, etc., resin oils, pine-wood oil, turpentine, aromatic hydrocarbons, carbon tetra-chloride, and camphor, soluble in water. The sodium salt of sulphonated palm oil mixed with citronella, gives a preparation useful in perfumery. The sulphonic acids or their salts may also be used in conjunction with a solvent, as detergents.

Waterproofing Chrome Leather. British Patent No. 16,060. E. W. TERRY, Victoria, Australia. The materials used are tallow and rosin, melted.

Producing Tanning. U. S. Patent No. 1,078,893. C. F. ALLEN, New Brighton, N. Y. The source of the tannin is pecan nut shells.

Work-Supporting Rolls for Leather-Working Machine. British Patent No. 21,618. H. A. HOLDEN, Lynnfield, Massachusetts. Pneumatic roll, same as U. S. Patent 1,067,607.

Leather Manufacture. British Patent No. 21,175. J. BYSTRON, TESCHEN, BOHEMIA, AND KARL, BARON VON VIETINGHOFF, Berlin. Iron-tanned leather is heated with solutions of basic alkali salts, or alkali bases or neutral alkali salts of strong acids, whereby some of the iron oxide is converted into an insoluble basic salt which imparts softness to the leather. The leather is treated so as to be as basic as possible, for which purpose basic alkali salts, such as borax, soda, sodium hydrate, etc. are preferably used.

Digitized by Google

The leather may be fulled in a concentrated salt solution, or the solution may be applied to the surface of air-dried leather. After the salt has acted, it may be removed simultaneously with the existing acid iron salts by washing the leather in water.

Waterproofing Leather, Etc. British Patent No. 21,081. A. McLERMAN, Ross, Hertfordshire. Leather is rendered waterproof and non-slipping by treating it with a mixture of rubber solution, celluloid solution, and gum juniper and resin in ether and benzol, etc.

BOUND VOLUMES OF THE JOURNAL.

Copies of Volume VIII of the JOURNAL, for the year 1913, are now ready, bound in cloth or half morocco, uniform with previous volumes. Price $6 per volume, delivered. Copies of all previous volumes may also be obtained. Bound volumes will be sent in exchange for sets of unbound numbers at the rate of $1.20 per volume, delivered. Missing numbers will be supplied at 25 cents each. Unbound numbers for exchange should be well packed and sent to the Manager at Ridgway, Pa., expressage prepaid at the "printed matter" rate.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. IX MARCH, 1914 No. 3

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1914, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VEITCH, . . . Past Presidents

OFFICERS, 1913-'14

PRESIDENT—W. K. ALSOP, Ridgway, Pa.

VICE-PRESIDENT—C. W. NORRIS, 80 South Street, New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

LLOYD BALDERSTON, Ridgway, Pa.

C. R. OBERFELL, Harrisonburg, Va.

T. A. FAUST, 323 Academy Street, Newark, N. J.

ELECTIONS.

ACTIVE

Calixto Giordanego, Cartagena, Colombia, South America.

ASSOCIATE.

Peter J. Schwab, 3333 N. Smedley St., Philadelphia, Pa.

CHANGES OF ADDRESS.

Samuel J. Hefti, to 12 West Kinzie St., Chicago, Ill.

E. J. Haley, to 82 Beaver St., New York, N. Y.

George W. Toms, Jr., to 79 Warren St., Stamford, Conn.

CORRECTION.

In the table on p. 72, February number, the figures of F. M. Loveland for myrobalan and quebracho are reversed. The figures of the second column should be in the fifth, and vice versa.

Digitized by Google

ADDITION TO METHODS.

The recent vote on addition to Methods resulted as follows:—

Total vote, 44; necessary to adopt, 29; affirmative votes, 38; negative votes, 6. The addition is adopted, and is in force on the publication of this notice.

The addition is as follows: "When materials containing sulphite-cellulose extracts are analyzed, the fact that the material contains sulphite-cellulose extract shall be noted on the report."

H. C. REED, *Secretary.*

PROPOSED ADDITION TO METHODS.

The following paragraph has been submitted in writing to the Secretary in accordance with paragraph 23 of the By-Laws of the A. L. C. A. It is proposed to follow that recently adopted in regard to reporting analyses of materials containing sulphite-cellulose.

Proposed paragraph. The test for the presence of sulphite-cellulose in a liquor or extract shall be as follows: Five cc. of a solution of analytical strength shall be placed in a test-tube, 0.5 cc. of aniline added and the whole well shaken; then 2 cc. of strong hydrochloric acid added and the mixture again shaken. If at least as much precipitate remains* as is obtained when a comparison solution prepared as below is similarly treated, the material shall be held to contain sulphite-cellulose.

* Neradol D gives the same reaction.

The comparison solution shall consist of sulphite-cellulose in the proportion of one part total solids to 2,000 cc. of solution, and as much tanning material, similar to that being tested, but known to be free from sulphite-cellulose, as will make up the solution to analytical strength.

The member submitting this proposed paragraph explains the method of making up the comparison solution by stating that the amount of precipitate given by a water solution of sulphite-cellulose extract having 1 gram total solids to 2,000 cc. of solution is much less than that given by a solution which contains in addition to the sulphite-cellulose a vegetable tannin. To use the

Digitized by Google

solution having the sulphite--cellulose alone would therefore make the chemist liable to condemn chestnut extracts in which there is no foreign material.

PENTOSES IN TANNING MATERIALS AND THE DETECTION OF MANGROVE.

By H. C. Reed and Adolf Schubert.

Two papers have recently been published on this subject, one by George A. Kerr (JOURN. A. L. C. A., Vol. IX, No. 1, p. 25) and the other by J. L. van Gijn and H. van der Waerden (*Collegium,* No. 524, p. 639), the translation of the latter appearing in the JOURN. A. L. C. A., Vol. IX, No. 2, p. 109.

Some little work has been done in this laboratory in the direction of confirming the work of the authors quoted and with especial reference to the dependability of the method suggested for the detection of mangrove extract in admixture with other tanning extracts.

Considerable research had been done before the article of van Gijn and van der Waerden had come to the notice of the authors, principally along the lines of determining the source of the furfurol production from the distillation of tanning extracts with diluted hydrochloric acid.

That the pentose sugars will yield furfurol by distillation with weak acids is noted by van Gijn and van der Waerden as proved by the investigations of Tollens, de Chalmot, Cross and Bevans and others, who have found other compounds besides pentoses in plants which yield furfurol under similar conditions. Furfurol is precipitated by phloroglucin as furfurol phloroglucid, a black precipitate, the solution immediately turning yellow upon addition of the phloroglucin and then rapidly green before the appearance of the precipitate.

Tests made with the pentose sugars, xylose and arabinose by distillation with 12 per cent. hydrochloric acid, confirmed the statements made as to the production of furfurol, and also by the distillation of rhamnose, a methylpentose (isodulcite), it was found that methylfurfurol was obtained, giving a yellow solution

Digitized by Google

upon addition of phloroglucin which threw down a brick-red precipitate. We find that filter paper steeped in aniline hydrochloride gives, with furfurol, an immediate cerise coloration while with methylfurfurol it gives a yellow coloration turning to brick-red. We desire to make it clear that the yellow coloration followed by a red precipitate upon addition of phloroglucin to the hydrochloric acid distillate is not necessarily an indication of the presence of methylfurfurol, since other aldehydes, formic, acetic, anisic for example, give the same test. At the same time the aniline hydrochloride saturated paper apparently distinguishes between methylfurfurol and the other aldehydes, anisic aldehyde giving a yellow not turning to crimson, acetaldehyde and formicaldehyde no coloration and paraldehyde showing crimson coloration.

It might very readily be concluded from the paper of van Gijn and van der Waerden that pentoses, pentosans and methylpentoses existed as such in tanning extracts, but we desire to point out that this is not by any means necessarily true. Pentoses and methlypentoses may be formed during the hydrochloric acid distillation itself, by hydrolysis of glucosides and other materials present, and as will be shown later this is almost certain to be the case with some tanning materials. Furfurol is quite generally produced by the breaking down of carbohydrates under the influence of boiling dilute acids; and methylfurfurol, since it is formed by hydrolysis of rhamnose with dilute acids, is naturally produced when materials are present that split up under the influence of acids yielding rhamnose as one of the products. Thus quercitrin, sophorin, the glucoside of blackthorn berries, xanthorhamnin, hesperidin, frangulin and probably many other glucosides break down yielding rhamnose. To digress somewhat, we believe that the fact of the breaking down of glucosides in the manner indicated introduces an error into the determination of the sugar content of tanning materials, since the sugars present as ascertained by hydrolysis of the material include the sugars formed in the operation itself and not naturally present as such. Thus xylan, or wood gum, yields xylose, a pentose sugar which reduces Fehlings solution, when boiled with dilute

Digitized by Google

acids. The pentose sugars are not fermentable and therefore have no part in the production of acid.

Distillation tests were run with hexose sugars to ascertain whether these gave with the phloroglucin test reactions similar to those from the pentose and methylpentose sugars. We find that dextrose in large amount gave a reaction similar to methylpentose, *i. e.*, the methylfurfurol reaction, and in small amount a negative test, while levulose in all amounts a negative test. The amount of dextrose necessary to give the phloroglucin reaction for methylfurfurol is entirely too great to admit the possibility of its being the cause of the reaction given by mangrove extract.

Tests were run on commercial extracts to ascertain the accuracy of the method proposed for the detection of mangrove. We find that the following extracts give the furfurol reaction with phloroglucin; quebracho, both ordinary and sulphited, myrobalans, sulphite-cellulose, sumac and chestnut. Gambier gave a slight drab-colored precipitate with a colorless solution, showing the absence of pentose or methylpentose sugars or of glucosides or other materials that yield these sugars by hydrolysis. As sugars are present in gambier in rather considerable amount it might well be argued that they are in the form of hexoses and that this material would ferment readily to form acid.

Commercial mangrove extracts tested gave the methylfurfurol test upon distillation with hydrochloric acid, but we desire to note that the precipitate obtained with phloroglucin was not of the distinct brick-red color given by the methylfurfurol phloroglucid obtained from rhamnose, but was distinctly of a brown color.

The lack of the distinctive brick-red colored precipitate in the case of the commercial mangrove extract led us to believe that the distillate might possibly contain a small proportion of furfurol. On this theory extractions were run on mangrove barks, both fibrous and non-fibrous, by the following methods:—

1. Cold water extraction.
2. Hot water extraction, official method.
3. Pressure extraction, 150° C. sealed tube, 4 hours.
4. Hot water extraction, collected all outside.

Digitized by Google

The extractives in all cases were filtered to remove traces of bark, and evaporated to dryness.

The hydrochloric acid distillate from the extract, from (1), gave the yellow coloration with red-brown precipitate in the case of the non-fibrous bark, the precipitate more nearly approaching in color that obtained from the distillation of rhamnose, while the extract from the fibrous bark gave tests practically identical with those from the commercial mangrove extract. By method (2) the phloroglucin precipitate was decidedly green, turning black upon standing in the case of both barks.

By method (3) the yellow coloration of the solution upon addition of phloroglucin turned green almost immediately and gave the black precipitate as shown when furfurol is present.

By method (4) the results were identical with those from a commercial extract. Tests were also run upon an extract made by the extraction of a spent mangrove bark, and in this instance not the least indication of the characteristic color of solution or precipitate, shown by methylfurfurol could be observed.

It was thought possible that the methylpentoses might be split up into pentoses under the influence of temperature and pressure, and tests were made by employing Method (3) on a solution of pure rhamnose, but on distilling with acid in the usual manner no furfurol test was given by the distillate.

Quebracho wood was extracted by Method (1) and the phloroglucin test gave results almost identical with those from a commercial mangrove extract. Upon standing the color of the precipitate was perhaps a trifle darker than shown in the case of the mangrove.

From these results we argue that the character and method of extraction has a decided influence upon the test. In other words the green or yellow coloration and black, red or brown precipitate depends altogether upon the proportions of furfurol and methylfurfurol present in the distillate and this in turn depends upon the degree of extraction. Methylpentoses or methylpentose-forming compounds are apparently more readily extractable from the materials containing them than are pentoses or furfurol-forming compounds.

Since quercitrin, a glucoside, forms rhamnose on boiling with

Digitized by Google

dilute acids, it was argued that black-oak bark, quercitron, should give the test for methylfurfurol upon distilling with hydrochloric acid. Upon this supposition quercitron bark was extracted by methods 1, 2 and 4 as in the case of the mangrove barks, and with results by the phloroglucin reaction practically identical with those from mangrove. The reactions whereby methylfurfurol is produced from quercitrin are as follows:—

$$\underset{\text{Quercitrin}}{C_{36}H_{38}O_{20}} + H_2O = \underset{\text{Quercitin}}{C_{24}H_{16}O_{11}} + 2\underset{\text{Rhamnose}}{C_6H_{12}O_5}$$

$$\underset{\text{Rhamnose}}{C_6H_{12}O_5} = \underset{\text{Methylfurfurfol}}{C_6H_6O_2} + 3H_2O$$

Cutch, from the Acacia Catechu wood, is stated to contain quercitin (Loewy, Fr. 12,127) and hence probably quercitrin. A known sample of pure cutch gave results almost exactly similar to those from mangrove.

In all the hydrochloric acid distillations due precautions were observed to prevent entrainment and the distillates were passed through filters before testing. It was observed that in the case of mangrove, quercitrin and cutch there was a distinct yellow coloration of the distillate.

Attention is also directed to the fact that the velocity of the phloroglucin reaction is greatly intensified by the addition of large excess of concentrated hydrochloric acid. This confirms E. Lazar (L. F. Wensel, Univ. Vienna, Monatsh., 34, 1913-55).

We would say in conclusion that the results of this investigation seem to throw some considerable doubt upon the value of the proposed test for distinguishing mangrove extract in admixture with other tanning extracts. It would appear entirely feasible to produce an unsophisticated mangrove extract that would give a reaction so nearly similar to that given by other materials such as quebracho, myrobalans, chestnut, etc., as to make its detection altogether problematical.

Further work is under way with especial reference to isolation of the material which gives methylfurfurol on distillation of mangrove with hydrochloric acid, and we hope to be able to publish the results of this further research shortly.

TANNING RESEARCH LABORATORY.
New York, N. Y.

Digitized by Google

DETERMINATION AND ESTIMATION OF TANNING MATERIALS IN ADMIXTURE.

By Roy H. Wisdom.

In the announcement of Committee appointments for 1913, this subject was left open with the request for individual contributions.

The method which follows is a combination of Professor Procter's well-known qualitative reactions and some little research done by the writer, which combined, presents old principles to advantage and forms a method for determining qualitatively which is simple, short, and to the writer's mind at least, practically accurate in the case of all the better known tanning materials.

The following tanning extracts were used in the tests, care being of course taken to secure absolutely pure extracts. These various extracts, which are all commercial products and obtained on the open market, were, with the exceptions of gambier and sulphite-cellulose, checked with extractions from the raw materials. The wattle bark tests were obtained from the raw material. The list is as follows:

Quebracho—unclarified.
Quebracho—clarified.
Chestnut.
Oak Bark.
Hemlock.
Mangrove.
Myrobalans.
Valonia.
Divi Divi.
Wattle Bark—raw material.
Gambier.
Sumac.
Nut Galls.
Sulphite-cellulose.

The extracts were dissolved to approximately official analysis strength and cooled to room temperature. Two hundred cc. of each solution were then transferred to bottles of ample capac-

Digitized by Google

ity and to each bottle was then added 5 grams of pure degummed or boiled-off silk and allowed to stand over night with frequent shaking for a time shortly after immersion. In the morning the silk was squeezed as dry as possible by hand and the drying finished in an air oven. A comparison of the colors is herewith shown in the following table:—

NATURAL COLORS.

Extract	Color
Quebracho—unclarified	Flesh
Quebracho—clarified	Cream to light cream
Chestnut	Light brownish yellow
Oak bark	Reddish yellow
Hemlock	Light salmon pink
Mangrove	Light red
Myrobalans	Light cream
Valonia	Cream
Divi divi	Light yellow
Wattle bark	Light pink
Gambier	Yellow
Sumac	Light cream
Nut galls	Flesh
Sulphite-cellulose	Reddish cream

One advantage of this method is that it brings all the tanning materials to a comparative color basis. In other words, various makes of the same tanning material vary very little from the standard for that material.

Using reagents shown in the following table it is possible to go still further in the identification by simply dipping a small piece of the impregnated silk in the solution, washing, and comparing the resulting color with the standard.

The various colors, especially those from the lime water, should be allowed to develop.

In conjunction with the above, Professor Procter's tests are carried out on the fresh solutions. With these various deductions, it is possible to arrive at a practically accurate estimate of the tanning material constituents of the extract in question.

Some of the tanning materials have extremely distinctive tests which are familiar to most of the trade chemists. Others show no particular individuality, falling more or less into groups, and it is to this class that the above method is particularly adapted. As an example, mangrove which has always been more or less

Digitized by Google

Material	Lime water saturated	$SnCl_2$ ¼ per cent. solution	$CuSO_4$ ½ per cent. solution	Na_2CO_3 ½ per cent. solution
Quebracho—unclarified	Light salmon	Dull yellow	Light tan	Pink
Quebracho—clarified	Reddish cream	Canary yellow	Light olive	Light pink
Chestnut	Dark olive brown	Brownish yellow	Yellow brown	Tan
Oak bark	Red brown	Yellow brown	Brownish yellow	Reddish yellow
Hemlock	Red brown	Light pink	Light pink	Dirty pink
Mangrove	Deep red	Salmon	Light salmon	Salmon
Myrobalans	Olive	Light yellow	Reddish yellow	Yellow cream
Valonia	Dark drab	Cream	Light tan	Tan
Divi divi	Yellow brown	Dull yellow	Reddish yellow	Yellow
Wattle bark	Dark brown	Flesh	Buff	Light tan
Gambier	Reddish yellow	Brownish yellow	Dull yellow	Reddish yellow
Sumac	Light olive	Cream	Dull yellow	Light yellow
Nut galls	Cream	Flesh	Cream	Cream
Sulphite-cellulose	Reddish cream	Brownish yellow	Reddish yellow	Flesh

Digitized by Google

of a stumbling block, gives a very characteristic reaction with the silk-lime water test which was shown by no other tanning material tested in this laboratory. If these tests are carefully interpreted, there are very few tanning materials which will escape detection in the ordinary run of commercially blended extracts.

CONTRACT ANALYSES.

By Oma Carr.

Whatever may be the short-comings of the present method for tannin determination when considered from the scientific standpoint, it may be fearlessly recorded that from the commercial point of view the method has reached a stage in its development where it may be deemed entirely competent. While working chemists may have occasional instances of wide variation to plague them and their clients, and ever and anon the impatient unbeliever may shout anathema, the clean, clear fact remains that there is sufficient measure of dependability in the method to justify hard-headed (mayhap frequently muddle-headed) business men in making it the basis for the settlement of dollars-and-cents affairs.

In the purchase and sale of tanning materials the method has become indispensable—and the word is used with complete deference to its scope. Narrowing the application to extracts, it is safe to say that well beyond 90 per cent. of sales involve adjustment through analysis—the immediate and imminent measure of value between buyer and seller. Perhaps there was a time when the tanner had hopes that the method would give him a direct and final appraisal of his extract in terms of exact leather making capacity, and the extract producer would have welcomed a similar result; but gradual realization of the complex factors involved in such appraisal brought both tanner and extract maker to acceptance of the method as it stood—a measure of hide-combination capacity. Thereupon the use of the method in commercial transactions reached wide limits, practically all tanning materials being bought and sold on tannin content, as determined under the Official Method.

As examples of the dependability of the method for large commercial transactions, the following instances are noted:

Digitized by Google

Adjustment A.—In this instance 33 cars of powdered chestnut extract were embraced, two chemists working on works sample; and when it is considered that this material is one of the most difficult for the chemist to handle, the results are striking:

	Chemist A	Chemist B
Car 1	62.38	61.68
2	61.90	62.10
3	65.94	65.58
4	64.92	65.83
5	66.40	66.59
6	66.05	66.04
7	69.28	69.97
8	62.83	62.83
9	61.11	60.91
10	68.10	68.05
11	65.83	65.42
12	64.67	64.60
13	63.20	63.10
14	62.62	62.81
15	64.27	64.12
16	65.88	65.76
17	62.56	62.53
18	63.97	64.01
19	63.85	63.93
20	64.71	65.41
21	65.33	65.46
22	64.80	64.66
23	67.69	67.56
24	66.81	67.03
25	70.06	70.11
26	71.20	71.45
27	71.22	70.22
28	70.46	70.42
29	70.44	70.36
30	66.78	66.93
31	67.28	66.52
32	65.81	66.03
33	66.57	66.88
Averages	65.91	65.91

In this adjustment the number of tannin units was calculated in each car, and the true value of the car thus ascertained. The extract was invoiced on the analyses of Chemist A, the contract providing for adjustment on the average analyses of Chemist A and Chemist B. As the cars were not equal in weight, the total

Digitized by Google

tannin units as ascertained from the invoice analysis varied, in value, from those deduced from the average analyses, by $7.99—on merchandize the total value of which was about $62,000. Counting the cost of the analyses at $200, tabulation at $15 and adjustment at $8, the total cost of controlling this adjustment may be taken at $223, or 0.36 per cent. of the value of the merchandize. As this form of adjustment is automatic, requiring neither time nor trouble on the part of buyer and seller, it may be regarded as commercially perfect.

Adjustment B.—This contract covered liquid extract, 26 cars being embraced in the adjustment period; it differs from Adjustment A in that the analyses were by one chemist, but working on samples drawn at works and at tannery. Invoices, however, were based on analyses by Chemist B, final adjustment being made under the analyses by Chemist A:

	Chemist A			Chemist B
	Works sample	Yard sample	Average	Works sample
Car 1	28.74	28.99	28.87	29.05
2	30.90	30.68	30.79	31.12
3	28.62	28.31	28.47	28.91
4	26.84	27.28	27.06	27.57
5	30.47	30.41	30.44	30.12
6	28.08	28.02	28.05	27.63
7	28.67	28.63	28.65	28.77
8	28.86	29.05	28.96	29.17
9	29.36	29.53	29.45	29.36
10	29.93	29.93	29.93	30.47
11	28.04	28.01	28.03	28.04
12	30.30	30.00	30.15	30.15
13	30.33	30.50	30.42	30.17
14	30.78	30.36	30.57	30.74
15	26.52	26.34	26.43	26.55
16	31.28	31.34	31.31	31.24
17	32.38	32.24	32.31	32.02
18	30.44	30.24	30.34	30.50
19	29.00	29.33	29.17	28.98
20	31.98	32.14	32.06	32.13
21	31.08	31.11	31.10	30.94
22	25.23	25.02	25.13	26.01
23	25.97	25.63	25.80	25.99
24	29.46	30.08	29.77	29.68
25	29.22	30.07	29.65	28.81
26	29.10	29.16	29.13	29.13
Averages	29.30	29.32	29.31	29.35
Merchandize value	$31,945	$31,968	$31,955	$32,000

Digitized by Google

This adjustment merits special attention because the referee chemist worked upon samples drawn at two points—shipment and delivery—the samples reaching him at considerable intervals. Also, the results are distinctly complimentary to the yard sample—which, it should be noted, was in this instance taken with scrupulous care and attention to details; proof that the works and yard samples can be made to agree when proper sampling is followed.

Adjustment C.—On 44 cars liquid extract, sold on guarantee of 25 per cent. tannin content; works sample governing, average of Chemists A and B:

	Chemist A	Chemist B
Averages	25.22	25.18
Merchandize value	$53,000	$52,915

Adjustment D.—On 72 cars powdered extract, unit basis, average of works and yard samples, by Chemist A, invoices on analyses of works sample by Chemist B:

	Chemist A		Chemist B
	Works sample	Yard sample	Works sample
Averages	66.68	66.59	66.60
Merchandize value	$137,164	$136,989	$137,000

Summary.—In these four adjustments the merchandize value involved totals $284,164 maximum, $283,841 minimum, or a widest difference of $323 on such very large totals—about 0.11 per cent.; and it should be remembered that 70 per cent. of the material was powdered extract, which is much more difficult of analysis than the liquid.

Commercial results such as those cited justify the conclusion that for extract contract purposes the Official Method has been brought to a satisfactory degree of accuracy.

Digitized by Google

WATER AND ITS PURIFICATION FOR TANNING PURPOSES.*

By M. F. Corin

Mr. President, and Members of the Association: The subject of water and its purification for tanning purposes in my opinion is a subject which is very great in every meaning of that word, and I do not think that it is possible for us to discuss the subject in the way in which perhaps it should be done. It is my special object in this paper to give you gentlemen some food for thought. At the same time I shall point out to you a few possibilities which might be utilized for the tannery. I have not heard, I think, of any case yet, where the tanner has gone to the trouble to really find out what he can do for himself and thereby cut down the expenses in making his leather, when the question of water comes in. I hope I am greatly mistaken, however, on that point.

In the past when it came to decide the location of a tannery one of the first matters to be taken in consideration was the water. There was a time when a tannery would have been an impossibility in certain locations, on account of the character of the water obtainable. To-day, however, thanks to the progress made by the ever-searching chemist and engineer, we have developed a knowledge of water and its purification which makes it possible to make a statement, that within reasonable limits, there is no water which is so bad from a tannery chemist's point of view that it would not be practicable to purify the same sufficiently to make it fitted for tanning use. This in itself is quite remarkable. However, the knowledge of the chemical engineer and water experts goes even so far as to make it possible without the use of fuel or chemicals to convert a water hardly fitted for tanning purposes into one upon which it is hard to improve by methods which are almost entirely automatic.

Although it is not an unusual thing that the water is blamed for a great deal of the trouble that a tanner is up against, one is ofttimes justified in saying that in spite of all this the question of water is not given the kind of consideration it deserves. I mean to say that the tanner should not be satisfied with just say-

* Read at the A. L. C. A. Convention, Atlantic City, Dec. 6, 1913.

Digitized by Google

ing unkind words about his water supply until he knows that the water has been given all due consideration from a chemical engineer's point of view and that it is not possible to improve upon the same. Taking into consideration the very large quantities of water used in a tannery, the magnitude of its importance may be realized. A comparatively small amount of hardness or iron present will in the end make a great deal of difference. The opinion as to the effect of the impurities in water differs to some extent, but on the whole we all emphatically agree that the purer the water the better all around and if it is possible to improve the quality of the water without any considerable expense, it should be done. Perhaps herein lies the answer to the question—Why does not the same material when used at different places produce the same quality of finished product when handled by the same man?

The cost of purifying water is now comparatively low, so that there are no very great arguments against it. Not doing it is a penny saved and a dollar spent.

The demand as to the quality of the water varies somewhat in the different departments of the tannery, but even so, there should be the same standard all the way through. Nothing but the best is good enough.

The water should be clean, that is, free from turbidity and contamination, soft and free from iron. Turbidity is due to suspended matter, inorganic and organic. Contaminated water is extremely objectionable. Hides may be quickly destroyed by the rapid action of the organisms in such water. That water is clear is not a guarantee against contamination. Well water is often found very treacherous. It might be highly contaminated though otherwise clear as a crystal. The color is from organic humus acid compounds and, as a rule, indicates presence of iron.

The turbidity and bacteria are removed by processes of sedimentation and straining, with or without the use of chemicals, depending upon the character of the suspended matter. The best and quickest results by these methods are obtained with the assistance of a coagulant, the object of which is to gather together the finer particles which are then quickly settled or retained on a filter. There are several water purification plants

Digitized by Google

where coagulation and sedimentation (settling) are entirely depended upon—there are others where only filters are used. However, the best way is the combination of both. Of the coagulants available for the purpose, the best and the safest for tanners use is sulphate of alumina. The success of this purification process depends upon the efficiency of the sulphate of alumina and its proper application. Added to the water in a 3 to 5 per cent. solution it reacts with the alkalinity (the temporary hardness) of the water, forming sulphates of the alkaline bases and a flocculent hydrate of alumina is precipitated. A coagulating tank or basin especially constructed is used for the purpose, and if of proper construction the precipitated alumina will have time to do its work as well as to settle out before the water gets to the filter which will remove what is left in suspension. The temporary hardness will be reduced in proportion to the amount of sulphate of alumina that is used. At times there is not sufficient alkalinity in the raw water to coagulate the alum and in such cases it is necessary to add slaked lime or soda ash. This is, as a rule, added ahead of the alum solution.

Another method which promises great possibilities for a tanner's use for purification of water is by the use of electricity, which will be mentioned later on.

The hardness of the water is mostly due to salts of lime and magnesia held in solution. We distinguish between the temporary hardness, by which is usually meant that part which is removed by boiling, and permanent hardness, mostly sulphates and chlorides which remain in solution.

For unhairing purposes the hardness means less than in any other part of the tannery. Where sodium sulphide is used alone, it would cause a proportionate waste of that material. For soaking, washing and bating purposes, as well as for use in the yard and leach house, the temporary hardness is a great disadvantage. If the hide taken from the lime is thrown in a water high in bicarbonate a corresponding amount of lime may be fixed as carbonate in the hide. The result will be the rough grain, and, when put in the liquors, stain and discoloration from formation of lime tannate which oxidizes when in contact with the air. In other words, poor looking leather will result. The lime once

Digitized by Google

fixed in the hides is hard to remove. It stubbornly resists the solvent effects of puering, bating and drenching. It is also liable to retard the process of puering. Hard water used in a yard and in the leach house will mean considerable loss of valuable tannin, as each part of lime will combine with many times its own weight of tannic acid which thus will be made useless.

The effect of hard water when used in the leach house, from my point of view is of very great importance and should be taken into careful consideration when looking for a water supply for use in the tannery. In connection with this I might mention what is going on in Germany to-day amongst the textile industry.

The textile industry suffers from the loss of soap when they are using the hard water. That soap costs them probably about 4½, perhaps 5 cents a pound. One of the large industrial corporations of that kind in Germany spent as much as $45,000 for erecting a permutit water softening plant to remove the last one degree of German hardness in the water, which represents about 17 parts per million as we count it. Just imagine what it would mean to the tanner who is losing his valuable tannin which is being neutralized by the lime in the hard water.

It is suggested that an acid is used to neutralize the temporary hardness. In such case it would be preferable to use an acid which forms an easily soluble salt and which would have no ill effects on the liquors, in case an excess is used. Lactic and acetic acids which are contained in the liquors suggest themselves on that account.

The effect of the permanent hardness is disputed, but it is generally agreed upon that minus the same we are much better off.

For boiler purposes both the temporary and the permanent hardness are very objectionable as they will precipitate from the heat in the boiler and form a hard scale unless the boiler metal is treated and made repellent to the scale-forming precipitate which in such a case will be blown out as mud instead of sticking to the metal as scale.

The hardness is very objectionable in making up the fat-liquors of soap and oil. For each degree of German hardness 1¼ pounds of soap will be wasted for every 1,000 gallons of water used, or about 2 ounces per 100 gallons. This should be

Digitized by Google

taken in consideration when preparing the fat-liquors. The lime soaps formed will adhere to the leather and cause trouble with the glazing. Sodium carbonate, though objectionable to some extent, in the same way as the bicarbonate of lime and magnesia as it will fix the lime in the hide, is, however, on the whole less objectionable.

Hard water is not suitable for dyeing purposes as it will precipitate the color base, making a total waste of that part of it. This precipitation will cause uneven dyeing and give rise to spots and streaks by depositing on the skins.

Iron is perhaps the most objectionable of the mineral impurities in water when used in a tannery.

I cannot allow more time to go into further details about the effects of hardness, etc., in the water and it is unnecessary as, undoubtedly, you are all pretty well familiar with them. I will instead devote the time to the methods which may be used to purify the water for overcoming these difficulties.

It would be best to remove the hardness altogether without leaving anything in the water which could have any disadvantageous effect. There are several old and some newer processes developed, depending upon the use of chemicals which react with the matter causing the hardness, precipitating it, and the removal of the precipitated matter through sedimentation or filtration. The chemicals used for the purpose of precipitation are usually slaked lime, sodium carbonate and alkaline hydrates. These processes do splendid work when properly applied and under the supervision of a chemist. The objection to such a process used by itself is the difficulty to control the chemicals used. As the raw water changes in any way, as it does in many places, the chemical treatment has to be changed accordingly, necessitating frequent analysis.

The success of these processes depends greatly upon the detail of construction of the apparatus used as well as the man in charge. The latest utilize the heat from the exhaust steam, thereby getting the water slightly heated, which considerably increases the efficiency. Instead of being intermittent processes as formerly they are now made continuous.

The very interesting process of water softening by means of

Digitized by Google

zeolite has been made possible by Prof. Gans, a German chemist who succeeded in producing an artificial zeolite by fusing felspar, kaolin, clay and soda. This zeolite has the characteristics of being able to exchange its sodium for lime and magnesia, etc. The result is that if a water containing lime and magnesia salts in solution is allowed to percolate through this mineral, all the lime and magnesia will be entirely removed by the formation of the lime or magnesia zeolite, and the sodium salts will go into solution. The zeolite, after its sodium is used up, is regenerated by allowing a 10 per cent. common salt solution act upon it, when the chlorides of lime and magnesia go into solution while the sodium zeolite is forming anew. This reaction can be repeated indefinitely. The wearing on the zeolite is practically none.

Reviewing these two processes mentioned, taking into consideration the disadvantages of both of them, as well as the advantages, one can easily see what splendid results can be obtained by the combination of the two. By first applying the chemical process and finishing up with the permutit process, we would be able to secure a water which would be entirely free from any hardness and also low in sodium carbonate. If there is iron to be removed, this would be done by use of the permanganated zeolite.

Where both hardness and turbidity are to be removed from the water there are convenient systms constreucted for the handling of such a water, which are recently developed and which are obtainable at comparatively small cost, compared with the costly apparatus which have been the only ones available up to rather recently.

Until recently it has been almost impossible to remove iron satisfactorily, but we know now how to remove even the last trace of it. This can be done by the use of manganese permutit (which is a zeolite in which the sodium is replaced with manganese by treatment with manganese chloride and potassium permanganate solutions) by simply allowing the water to percolate through it. The iron is completely oxidized and precipitated as hydroxide which will be entirely retained in the filter. When the oxidizing power of this prepared mineral is used up it is easily regenerated by a solution of permanganate.

Digitized by Google

In order to extend as much as possible the intervals between the regenerations, and to maintain the oxidizing power of the filter, a highly diluted solution of potassium permanganate is supplied, drop by drop to the water. This produces a fine precipitation of manganese hydroxide which causes the iron itself to separate out to a great extent. This also causes the greater part to collect on the top of the mass and it may be washed out by reversing the current of the water.

The electric process referred to is perhaps the one that has greater promises in store than any other process for the tannery, because it will remove turbidity, hardness and contamination at the same time without leaving anything in its place that would diminish the value of the process. This method has been laughed at, then accepted, then pronounced impracticable, all inside of a comparatively short time, but there are very good reasons to believe that a time will soon come when we have learned to overcome the difficulties which we were up against in perfecting a process of this kind. One of the difficulties of this system is to produce an electrode which is not too quickly consumed. The indications are that, in connection with a coagulating basin where sulphate of alumina is used, which would cosiderably reduce the cost of the treatment, this process will become a valuable asset to some tanners.

One of the greatest water problems now facing the tanner, and the solution of which is becoming more and more important, is the question of the waste water from the tannery, as the municipalities are strenuously objecting to the pollution and discoloration of the streams where the waste water is run. The inventor of this process claims that it will be possible to solve this problem by the use of electricity and to produce a water free from the objectionable matter to an extent great enough to make it unobjectionable to the municipalities.

DISCUSSION.

DR. ALLEN ROGERS:—I was "from Missouri" about this permutit until three days ago, when I saw a demonstration of the process, and am not "from Missouri" any longer. It certainly is a very interesting process and, I think, one that will appeal to the tanner.

Digitized by Google

MR. CORIN:—I have a print here, which will show one of the systems used for domestic purposes. It is just an iron tank with a few pipe connections and above is a tank where they have the salt solution. When the softening power of the zeolite in the filter is used up you just simply run the water out and the salt solution in. It takes about eight hours for the regeneration of that system. Then naturally the salt solution has to be removed by washing, fill it up with water about three times, or something like that, and it is again ready for operation.

MR. NICHOLS:—Mr. Corin's paper I think is unusually interesting, and it surely would be interesting to our tanner friends if they were here and heard that paper and heard it discussed. The subject of purifying water for a tan yard or an extract factory or for manufacturing of leather is a very essential thing, and especially the iron in the water, which no doubt is the cause of considerable trouble. In fact I have had a number of instances where I was called to tanneries to diagnose the trouble, and very often I have found iron to be the cause. Mr. Corin's paper covered the field of purifying water and removing the iron and so forth. I have done some work along that line, but I have carried my work a little farther than just the water. For instance, if wood is extracted with purified water the tanning material adds to the water some of the impurities that you had in your water before starting, but of course not quite so much. In extracting a wood, the water takes iron out of that wood, and also lime. The tanner carries these over into his tan yard and he has those same ingredients that give him trouble in the water and it occurred to me that it would be a good plan to try and go farther than just the water used in leaching, for instance, of barks and woods and to remove the iron from the tan liquor after the wood is extracted. I do not know whether any chemist here present has tried to remove the iron from tan liquors or not, but if you have, no doubt you have had some difficulty. I know I have run up against a great many difficult things in trying to get iron out of a tan liquor and not effect my tannin. During the last four years I have been working along that line, to remove iron from tan liquors without using chemicals, and I have succeeded lately in doing so, and I believe the process could be

Digitized by Google

applied to the tan liquors in the tan yard, and as Mr. Corin says, it could be applied to the water before extracting the tannin and keep that much out; but if any chemist has worked along that line and has tried to throw iron out of a tan liquor without affecting the tannin or using any chemical and has had no difficulty, I think he is very fortunate. I think I have made something like a thousand experiments along that line within the last four years and I finally have got this in such a condition that I can remove the iron from the tan liquor without using any chemicals, and I hope in a future paper to present the process before the Association. The only thing I have at present is some small skivers I have tanned from these liquors after removing the iron.

MR. CORIN:—It might be interesting for the Association to know that Mr. Oberfell and myself have decided to work out "the effect of impurities in the water on the tanning of leather from an economical standpoint." In other words, instead of just telling you what can be done and should be done, we will endeavor to give you the figures showing why it should be done.

MR. VEITCH:—I think the fact that artificial zeolites can be readily made was discovered by the agricultural chemist something like 60 or 70 years ago, and the importance of this reaction in agricultural chemistry was then thoroughly pointed out. It is very interesting to note that it has taken 60 or more years to get an industrial development of this important matter.

MR. CORIN:—Well, Mr. President; It might be interesting for you to know that the reason why it has taken such a long time to make a commercial proposition out of this, is the great difficulties which had to be overcome in the making of that preparation successfully in a commercial way. We have known of zeolites for, I guess, more than 60 years, and we have been trying to make them for a great many years, but we have not been able to do it successfully in a commercial way until Doctor Gans succeeded in doing so. I understand from the information that I have been able to get that he is the man who took out the patents for the process which is now used in Germany, and which I understand will be utilized here in the United States very shortly. I understand they are building a plant for making zeolite over here. So far it has been imported from Germany.

Digitized by Google

MR. KERR:—I would like to ask, what is the cost of the material and what has been your experience with reference to the settling of the precipitated materials in a treated water; say in a 25,000 gallon tank how long should it stand before removing?

MR. CORIN:—Well, as to the cost of the zeolite, I know nothing about it. As far as the settling is concerned I presume you mean in connection with the chemical process.

MR. KERR:—Yes.

MR. CORIN:—Well, to-day fortunately we know or should know better than to use those old methods, because we have the continuous process where we filter away the precipitate. In other words, instead of having a large settling tank we have some kind of straining medium which removes the precipitated matter. I understood from one of my friends, from whom I got some information, that for $1500 he could put up a water-softening plant that would handle about 50,000 gallons a day. That is most remarkable to me, because up to that time I had been under the impression that it would cost about $3,000 or $4,000 at least for a plant of that size.

MR. OBERFELL:—You said in connection with the action of water on boilers, I believe, that if the boiler surface were properly treated the scale would not form. Do you know of any preparation that would properly treat the boiler tubes?

MR. CORIN:—Although that perhaps sounds impossible. I am glad to say that it really can be done. There is a preparation on the market which is called Tegu-Film. It is, I understand, mostly a mineral preparation which, if introduced with the feed water to the boiler while under operation, forms a protective film on the metal which makes the metal repel the precipitate so that, instead of sticking to the plates and tubes forming scale it will fall down to the bottom as a soft watery mud and be blown out as such, without danger of bagging.

MR. TEAS: I would not advise any tanners to use that. It is mostly graphite, and it will loosen up the tubes in your boiler head so you can't keep them tight. After you roll them three or four times you roll the edges off them.

MR. CORIN: Did I understand you to say that this preparation I mention is mostly graphite?

Digitized by Google

MR. TEAS:—I don't know whether it is the one you mention, but the one I know is on the market for that purpose is a graphite preparation that makes the interior of the boiler greasy.

MR. CORIN:—Well, in connection with that I am pleased to be able to tell you that this preparation was used before the graphite people started to make a very serious campaign in selling graphite. You are quite correct when you say that graphite could form a film on the boilers, and a very objectionable one too, because graphite will keep the water away from the metal and will cause blistering where too much of it is used. At the same time, while personally I am not a believer in graphite, I might truthfully say that graphite will do a certain amount of good in the boiler. If used in moderation, graphite has a tendency to make a soft mud of the precipitate; I mean to say, that as a rule it prevents the precipitate from hardening after it has dropped down to the bottom of the boiler, so that it may be blown out more easily; but graphite used in those small quantities will not and cannot prevent the formation of scale. I have seen instances where a graphite used in a boiler has mixed itself with the scale-forming precipitate and formed a scale which was a mixture of a small amount of graphite and the scale-forming precipitate, giving you a film on the boiler which is a great deal worse than the scale itself. However, I do not think this as a rule happens. The Tegu-Film boiler preservative, which I highly recommend, is a preparation that puts a mineral film on the boiler, not a graphite film. You can use graphite in connection with this preparation and the graphite will not get on the metal, because this repels the graphite as well as the scale-forming precipitates.

MR. A. ROGERS:—In this connection, there is a boiler compound on the market which it is claimed forms a mirror on the inside of the boiler tubes. I have never seen it work. I know, however, that it is sold and I have seen several samples of it. It is claimed by some engineers that it does form a mirror; you can almost see your face in it.

MR. KERR:—I have tried that as well as a good many others. In most cases it is largely a theory rather than practice. But I would like to ask with this preparation you speak of what hap-

Digitized by Google

pens in the case of a boiler with a scale on it before you apply this preparation?

MR. CORIN:—Well, the manufacturers of this preparation claim, quite correctly—I have seen it work myself—that it works underneath the old scale. Having a greater affinity to the metal than the scale-forming precipitate, it will work down underneath the scale and mechanically dislodge it from the metal. It sounds rather fabulous, but I have had several opportunities to see it done.

MR. KERR:—That is claimed for the mercury compound. I have seen scale on boiler tubes and heads you could not take off with a cold chisel. Apparently the scale and the metal were almost homogeneous, and I do not think there is anything in the claim that it would get between such scale and the boiler sheet.

MR. CORIN:—The people I refer to do not claim they can do it quicker than you can with a chisel. I think they claim it will gradually remove the scale. Putting anything in the boiler that will too quickly remove the scale from the metal, is a mighty foolish thing to do for more reasons than one. Perhaps the most important reason is that one might be liable for very heavy damages for killing the fireman.

MR. DICKERSON:—I concur with what Mr. Teas has said. My personal experience in using the graphite was rather disastrous. We got a pretty bad blister on the crown sheet and also loosened the tubes in the tube sheet. It has been my personal experience that an accurate and judicious use of simple soda ash and a blowing out of the boiler at frequent intervals will take care of the scale in the boiler effectively.

MR. CORIN:—Well, Mr. Dickerson, it might be interesting to hear what people in general say about the use of soda ash:—You are quite correct when you say that soda ash is in some cases a good thing to use in a boiler for that purpose, but the disadvantage in using soda ash is that it produces wet steam, and we know how wet steam decreases the efficiency of an engine—if the steam is used for power purposes—That is one of the reasons why the engineers always recommend the use of a super-heater. For instance, take an engine that is running non-condensing. If the steam is superheated the efficiency may be increased fully 25

Digitized by Google

per cent. When you are using soda ash what are you doing? You are increasing the amount of moisture in your steam. Soda ash is the worst thing we know of for priming the boiler. Where they have trouble with priming the boiler, you will as a rule find that there is a high content of sodium carbonate. Water high in soda is in most instances undesirable for boiler-purposes.

MR. DICKERSON:—It is very true that with a large accumulation of soda the water will cause priming of the boiler, but that is easily overcome by frequent enough blowing down of the boiler. Do it every night if necessary, and you will keep the soda down. If the boiler is not carrying a very heavy overload there is no reason why you should have wet steam in your engine. If it is carrying a very heavy overload you will be very liable to have priming under any condition even without the presence of soda.

MR. CORIN:—But in most cases, I am afraid, people who have power houses do not have enough boilers that they don't have to carry an overload.

MR. DELANEY:—I would like to ask Mr. Corin in this treatment of the water by the permutit method whether there is any scale-forming material left in the water after the treatment?

MR. CORIN:—Absolutely none.

MR. DELANEY:—Well, isn't it the experience of people that use water that does not have any scale forming properties at all, or less than fifty parts to the million, that the boilers corrode below the water line always?

MR. CORIN:—That is often quite correct. However, a permuted water will not have that effect, for this reason: when you take the lime out of the water you get the corresponding amount of sodium carbonate in its place, which will counteract the corroding effect of some "pure" water.

MR. KERR:—You have already stated that soda ash is the worst thing you can have.

MR. CORIN:—I don't say that the permuted water is always the best thing for the boiler, though as a rule it is. If you are going to use a very hard water for the boiler it might be better to first use the chemical softening process and then finish it off with the permutit system. When you use soda ash for a boiler

Digitized by Google

you are generally putting several pounds of it in there at a time. Then when you blow your boiler about three inches you fill it up again; and you put in some more soda ash; then you blow it another three inches and fill it up again and put in some more soda ash, etc. There will be a much more rapid concentration of soda ash than with the use of the permuted water.

MR. VEITCH:—I have had no personal experience with the Tegu-Film, but I do know in the Bureau we are often called upon to make many examinations of boiler compounds for the different departments of the Government, and the man who has charge of this work has developed some very strong personal opinions—some might even call it prejudice—on this subject; and I have heard him say often, based on his examination of the work he has done, that the best boiler compound is none at all but to blow it out very often. That is his conclusion after examination of many samples of water and of many so-called boiler compounds.

MR. KERR:—Confirming what Mr. Veitch says, an experience of about 20 years has made that obvious to me. I have never seen a scale in any of our boilers and do not expect ever to see a scale in them. We never use any boiler compound. They are blown out four times in 24 hours, and the boilers are not a bit corroded under the water or anywhere else.

MR. CORIN:—What is the hardness of the water you use in those boilers?

MR. KERR:—Practically nothing. It is soft water.

MR. CORIN:—Very soft water?

MR. KERR:—Very soft water. We are using as near to distilled water as you can possibly get in nature. It runs about 3 parts of total solids per hundred thousand. In our boiler house we have two boilers that have been working under those conditions night and day for about 20 years.

MR. VEITCH:—You are blowing your boilers about three times oftener than is necessary.

MR. KERR:—With a compound,—yes, we are.

MR. CORIN:—You are located in Lynchburg?

MR. KERR:—Yes.

Digitized by Google

MR. CORIN:—Well, I can recommend the Lynchburg water for the boiler. I know it myself very well. It is wonderful water really, one of the few places where they are having little, if any trouble. Otherwise, an experienced engineer is likely to say, "I don't know of the water that doesn't give some troubles in the boiler." I have never seen one myself, except perhaps the Lynchburg water, where a man would dare to make a statement that he is not having trouble of some kind where he is not using something in the water.—This is what we hear the engineers usually say: "I'll be 'blanked' if there is a water on earth that will neither scale nor corrode my boiler."

MR. KERR:—Lynchburg isn't alone in this remarkable thing. I can take you to fifty or sixty places throughout the Appalachian range of mountains where the water is practically distilled water.

MR. CORIN:—Well, I am very pleased to hear, Mr. Kerr, that you are familiar with locations where you can get a good water for a boiler. However, even if that is the case it doesn't mean that the others are in the same fortunate position.

MR. KERR:—But it means this, to get down to the very thing you are advocating, purify the water before you put it in the boiler.

MR. CORIN:—Exactly. That's right.

MR. KERR:—Don't put any scale forming water in.

MR. DELANEY:—I can concur with Mr. Kerr thoroughly. We have three plants and we have about 5,000 horse-power in the three plants. We blow our boilers down every six hours and do not put anything in.

MR. CORIN:—Do you know what it costs you to blow your boilers?

MR. DELANEY:—I don't know. We blow them down one gauge.

MR. CORIN:—That is 3 inches. Some time ago I read a paper on this subject before an Association in the south, and getting my data together I found that the blowing of a boiler means about 60 pounds of fuel for one gauge. Now the question is, which is the best thing for you from an economical standpoint? What you want to do is to operate your boiler as economically

Digitized by Google

as possible. Which is best for you to do, to use a little bit of Tegu-Film in your boiler, or something, that you know is not going to harm your boiler, that will cost you about 5 cents a day to apply, or blow 60 pounds of coal out of your boiler about every six hours?

MR. DELANEY:—We don't put any soda ash in because it might make our steam wet.

MR. CORIN:—Well, that is not an answer to the question.

MR. DELANEY:—No; we are simply satisfied with that treatment; we have been thoroughly satisfied.

MR. CORIN:—Well, you know, that is an old argument that does not go any more, that we are "satisfied." No man living has the right to be satisfied before he knows that he is doing the thing that brings most back to the pocketbook of his employer. That is my personal opinion about it.

(Further information in regard to the Permutit process will be found in the JOURNAL for August, 1912, pp. 423-9. Objections to it as a method for boiler waters are briefly stated in the abstract which follows.—ED.)

ABSTRACTS.

Feed-water Purification and the Permutit Process. DR. E. E. BASCH. *Chem. Ztg.*, 36, pp. 769-70. The author objects to the use of the term "purify" in describing processes which in taking materials out of water substitute other materials for those removed. A raw water containing 136 parts per million of calcium sulphate and 100 parts of calcium carbonate, after permutit treatment has 142 parts of sodium sulphate and 106 parts sodium carbonate, a total of 248 parts against 236 parts before treatment. The same water treated with lime-water and soda would have 142 parts per million of sodium sulphate, and if treated with lime-water and barium carbonate would be entirely freed from dissolved material. Water which has been treated by the permutit process has been softened, but not purified. The permutit company advise that 1 to 2 cubic meters be blown out daily from each boiler, and that it be emptied entirely every 6 or 8 weeks. The cost of the salt used is about 0.5 cent per ton of feed-water, and the loss of heat due to blowing off amounts to 0.75 cent per ton more. The total cost of the treatment is therefore about 1.25 cents per ton. The larger the quantity of salts dissolved in the feed-water, the more water and foam are carried into the steam, particularly in the case of locomotives, and this causes serious difficulties. The author quotes from the claims made by the owners of the permutit process, and contradicts several statements. He calls attention to the

Digitized by Google

injurious effect of dissolved soda on boilers, and concludes that for locomotives the permutit process is generally not satisfactory. L. B.

New Colonial and Other Tanning Materials. *Bull. Imperial Inst.*, XI, 401-28. Black Wattle Bark from the East Africa Protectorate: About 2,800 acres are planted; in 1911-1912 10 tons were exported. The chief sources for this bark are South Africa and Australia, which in 1911 exported 49,645 tons and 12,677 tons respectively. The bark yielded a rather soft leather of a pale pink color. A small lot of this East African bark brought £7. 10s. per ton in London. Some other samples were also found valuable and on analysis it was found that thick bark is almost invariably richer in tannin and of better color than thin bark and realizes better prices. Acacia Arabica Pods from the Sudan: These pods are used in the Sudan for tanning purposes where they are known as "Sant"; in West Africa they are known are "Gambia" and in India as "Cabul" pods. They contain on an average 30 per cent. tannin; it is, however, possible to considerably increase the amount of tannin by grinding the pods to a granular powder and sifting the product to remove seed and some of the fibrous matter which contains no tannin; the resulting product is called "sant grains." The tannin varied from 54.5 to 60.9 per cent.; it gave a faintly pinkish white leather of soft but firm texture. The whole pods yielded the same kind of leather. A sample of these pods from Northern Nigeria showed somewhat less tannin, 26.69 per cent., and yielded a pale, fawn-colored, but rather soft leather. A sample of these pods from South Africa only gave 19.6 per cent. tannin. A sample of Talh bark (red variety), the product of acacia seyal from the Sudan consisted of fibrous bark, contained 18.1 per cent. tannin, but the leather was too dark colored and red to be satisfactory. A sample of bark of A. longifolia from Cyprus showed 15.3 per cent. tannin and yielded a dull brown leather with a purplish tint. Acacia cyanophylla bark from Cyprus was poor in tannin and gave a rather harsh, dull brown leather with a purplish tint. Bark from anogeissus leiocarpa from Nigeria and the Sudan was not found to be rich enough in tannin (9.6-17.1 per cent.) Twelve samples of mangrove bark were obtained from South Nigeria but none of them was found rich enough to be worth exporting to Europe in competition with East African mangrove bark; some of the samples might, however, be suitable for the manufacture of mangrove cutch. Mangrove leaves from the East Africa Protectorate only showed about 8.78 to 9.13 per cent. tannin, and yielded a leather of poor quality; they also contained a large percentage of salt (sodium chloride). Mangrove Extract from Fiji: This is probably suitable for dyeing sails, fishing nets, etc., but not for tanning leather without decolorization; it contained from 55 to 66 per cent. tannin. Brachystegia Barks from Mozambique: Three samples contained from 13 to 18 per cent. tannin; the leather yield was of good quality. Dried leaves and twigs of Osyris abyssinica (= Colpoon compressum, Berg.) from the Transvaal gave from 13 to 25 per cent. tannin; but the material possesses no special

Digitized by Google

quality which would render it suitable for export to Europe; the leaves were generally found to be richer in tannin than the stems. "Subakh" bark from the Sudan derived from Combretum Hartmannium Schweinf, gave a light colored leather of poor quality (12.8 per cent. tannin). Aleuntes barks from Hongkong showed deficiency in tannin. Phyllocladus rhomboidalis bark (celery top pine) was too poor in tannin to be remuneratively exported, but could be used locally, or for the manufacture of extract. "Kumbuk" bark from Terminalia glabra from Ceylon was found suitable for light leather (27.2-31.6 per cent. tannin).

Phyllanthus Emblica leaves from Hongkong are said to be used as a black dye-stuff for silk; they produce leather of good quality. Divi-divi pods (caesalpinia coriaria) from the Gold Coast gave only 33.1 per cent. tannin, probably because they had been collected in an immature stage; they furnished a soft, pale-brown leather.

ALEX. F. FUERST.

Practical Bating and Puering with Oropon. *Leather Trades' Review*, Jan. 21, 1914. The JOURNAL does not ordinarily abstract unsigned articles of the kind published under the above title in the latest magazine number of the *L. T. R.*, but the matter of artificial bates is of so much importance that we present a résumé of the article, whose subhead is "A Tour of Important German Tanneries." At a factory making fancy upholstery leathers and enamelled and patent leathers for shoe, carriage and upholstery work, oropon and formic acid are used for deliming. A drum runs about three-fourths submerged in a pit. First the pit is filled with water at 80° F. and 13 lbs. of oropon added. The drum is run a few minutes to mix the liquor, then stopped and loaded with from 50 to 70 split hides, washed from the limes. After 1½ hours, the drum is stopped and the hides tested for lime with phenolphthalein. Complete deliming is not desired. When the hides are nearly delimed and are partly "fallen," the drum is stopped and the hides allowed to lie another hour in the bating liquor. They are clean and white, with a soft and silky grain. They pass from the oropon bath to the liquors. The bating liquor is strengthened with 4 lbs. of oropon and another pack put through. After three packs have been treated, the liquor is run away and a new one made up.

The writer next visited the works of Röhm and Haas at Darmstadt, a picture of which is given. The firm has a branch in England, one in France and three in the United States. The next place visited was a fancy leather factory at Frankfurt a. M. For the treatment of 150 calfskins 6½ lbs. of oropon were used, in a paddle. After running nearly 2 hours, the skins were found to be insufficiently reduced, and were run 15 minutes more. Skins puered with oropon do not need to be treated afterward with a bran drench to cleanse them, and thus time is saved. The finished leathers were soft and supple, and took dyes perfectly. The cleanliness of the factory is one of the features commented on. A glazed kid factory at Marktredwitz in Bavaria was inspected. One of the members of the firm had had experience in American methods of manu-

Digitized by Google

facture. The skins used are Cape goat. They are unhaired with sodium sulphide, which swells them considerably. From the unhairing bath the skins are put into an old bating liquor for an hour, being kept in motion all the time. They are then taken out, drained for an hour, and weighed. The quantity of oropon used is based on this weight, 1 lb. of oropon being put into the new bath for each 145 lbs. of skins. The bath is warmed to 100° F., and the skins paddled in it for about 3 hours. The strength of the fiber is not impaired in this process.

A tannery at Backnang, in Wurttemberg, where chrome kips and vegetable tanned upper leather are made, uses a new oropon bath for kips which are to be chromed, 1 lb. of oropon to 500 lbs. of skins, white weight. The old bath is used to bate hides intended for vegetable tannage, 1 lb. of oropon per 360 lbs. white hide being added. At a glove leather tannery in Karlsruhe, a new bating liquor is made up with 1½ lbs. of oropon to 100 lbs. of lamb skins. The skins are started by paddling in an old bate for ½ hour after washing from the limes. They are then transferred to a new bath and paddled for 2½ hours. The last factory visited was a large glove-leather tannery in Luxemburg. From the limes, the skins are here washed in weak solution of oropon to remove the surface lime, and are then placed in a liquor containing 1 lb. of oropon for each 50 lbs. of small skins. Half an hour in this bath serves to delime and reduce the skins.

Leather Trade School at Madras. CONSUL JOSÉ DE OLIVARES, Madras, India. From the report of the Superintendent of Industrial Education for the Madras Presidency are taken the following excerpts relative to a proposed leather school to be conducted under government supervision in the city of Madras:

Pending the erection of the proposed government leather trades school in Madras, Mr. Guthrie was sent to Bangalore to study the working of the Mysore tannery as typical of indigenous methods. While at Bangalore he introduced a considerable number of improvements into the methods of manufacture there, more particularly with regard to the proper use of modern tools and appliances. The Indian village tanner as a rule uses only one or at most two tools for all the different processes in his trade, and consequently wastes a great amount of time, to say nothing of the inferiority of the work done. Even in the more up-to-date factories in India much can be done in the way of making the labor more efficient by the use of modern tools for certain processes. The greatest improvements in the leather trade that have been made in Europe and America during the last few years have been in the processes of finishing leather, and very much can be done in India in teaching how to give a finer appearance to the finished material. One of the greatest difficulties met with in Bangalore and elsewhere in India is to keep the grain of chrome-tanned hides tight, and during his stay in Bangalore Mr. Guthrie did much work on this subject, with fairly satisfactory results. At least one class of leather the dressing of which was taught to

Digitized by Google

the staff and workmen at Bangalore is now a regular line and is commanding a ready market. Fresh outlets for certain classes of hides that did not admit of working up in the ordinary manner were considered and in some cases discovered, and it is just possible that an export trade may be established that will prove to be a paying outlet for the excess of certain classes of leather for which the demand is not great in India.

So far as the leather trades school is concerned, the erection of the buildings has been delayed to some extent, owing to several causes. The plans, however, have already been prepared, and it is hoped that work will soon be started. During the year a considerable number of applications were received from students in different parts of the country for admission to the school, and it may be supposed that the new school will enjoy the same degree of popularity as the old one formerly carried on in connection with the government chrome tannery at Sembium. As is usual in India, a large number of the applicants for admission are men who, although possessing literary qualifications, have no connection with the trade and have no prospect of turning their knowledge to good account afterwards. As far as possible, it is intended to limit training to such individuals as can show that they have reasonable prospects of employment after completing their course of instruction. It is expected even with this limitation sufficient pupils will be forthcoming to make the school of material benefit to the leather trade generally. Another feature of the school will be that special arrangements will be made to teach "maistries" or workmen how to carry out work in connection with any process and how to use new tools or machinery.

Much research in connection with the leather trade has, of course, already been done in Europe, but the results are not, in general, applicable to India. The temperature conditions differ so enormously with two countries that a repetition of experiments is essential. Such work will be undertaken in the laboratory.

During the year the Inspector General of Forests came to Madras with a view to inquiring whether anything can be done in the manufacture of tanning extracts, and this question the leather expert has been engaged in considering. As a result of his inquiries it has been decided to associate with the tannery a bark yard where extraction experiments may be carried out, and these are likely to lead to useful results. Most of the failures in extract manufacture in India have been due to the extract having been made from materials without sufficient knowledge of the peculiarities of those materials. These can only be determined by careful laboratory tests previous to extraction and concentration. In other cases the results have not been as good as they might have proved had the experimenter known exactly what was wanted and had he been able to test the resulting extracts himself instead of having to send them to tanners for experiment and report.

Free Sulphuric Acid in Leather. M. JALADE. *La Halle aux Cuirs*, Technical Part, Dec. 21, 1913, and Jan. 18, 1914. [The title of this paper is

Digitized by Google

"Contribution to the Study of the Determination of Free Sulphur in Leather by the Process of Balland and Maljean." Since the substance determined in every case is free SO_3, and not free sulphur, I have taken the liberty of changing the title. Monsieur Jalade is chief of the chemical laboratory connected with the French army store-houses at Vanves.—*Translator.*] The method of Balland and Maljean consists in ashing samples of the leather with and without carbonate of potash. The SO_3 in the ash is determined by precipitation as barium sulphate in both cases, and the difference between the two is reckoned as free acid. The authors of the method recommend that 0.18 per cent. H_2SO_4, reckoned on the dry leather, be deducted from the total free acid as due to the sulphur normally contained in hide. The author directed his research first to determine the effect of the method of dividing the sample. He experimented with planed samples and those cut up with a microtome, the shavings being cut up with scissors. Thirteen leathers were examined, the total ash of which ranged from 0.46 to 3.07 per cent. In every case the SO_3 figure was greater where the sample had been planed into thin shavings. (There is one apparent exception, but the context shows that it is due to a typographical error.) In the extreme case the figure for free SO_3 is 0.82 per cent. for the shavings and 0.36 per cent. for the slices (not over 1/50 inch thick). The closest agreement is 0.25 per cent. for shavings and 0.21 per cent. for slices.

The second point examined was the effect of quantity of alkaline liquid used. The solution used contained 1 per cent. of K_2CO_3. The quantity of leather in each case is about 5 grams. As showing that this research was necessary, the author quotes results from two experts on five samples, identical in every respect including preparation. The results of one expert for free SO_3 are in every case more than twice as great as those of the other. Samples prepared in various ways were treated with from 10 to 40 cc. of 1 per cent. potassium carbonate solution. Other things being equal, larger SO_3 figures were given by larger quantities of solution. Another point examined was the effect of different solvents in degreasing the samples. No difference due to this cause was found. The time of standing with the alkaline solution before being put in the oven to dry was found to have no appreciable effect on the result. It will be recalled that some previous investigators have specified that the incineration must be done with an alcohol lamp, in order to avoid possible addition to the sulphur content of the ash by sulphur from the gas flame. M. Jalade concludes that this source of error is negligible unless the heat is very high and long continued. Results are summed up as follows: If the method is followed in a precise manner, including exactly similar division of sample, quantity of potash solution, etc., the results will be comparable and correct. The use of the plane is recommended, and the employment of a sufficient volume of alkaline liquid, in which case a correct value is assured.

[The author does not discuss the inherent weaknesses of the method. Thus if the leather contains Epsom salts, the sample ashed without

Digitized by Google

potash will lose more or less SO_3, depending on the heat employed, and this will appear in the result as free SO_3. So far from giving dependable results if carefully carried out, many experienced leather chemists in America are convinced that in most cases the method is quite worthless.—*Translator.*] L. B.

Cattle Industry in Paraguay. By JULES FRONTANILLA, of Assomption, Paraguay, pupil at the Tanning School at Liège, in *Bourse aux Cuirs de Liège,* Jan. 18, 1914. The following figures give an idea of the quantity of hides procurable from Paraguay and their approximate prices. In 1909 it was estimated that there were nearly 8,000,000 cattle on the pastures of Paraguay. Formerly cattle were imported from neighboring countries but now they are exported. The most successful society for this purpose is "La Foncière du Paraguay," with a capital of 3,000,000 francs, 14 establishments, 130,000 head of cattle and 3,500 horses. This society imports Hereford, Durham and Holstein bulls for breeding. An average price is about 82.50 francs ($16.50) for steers and 70 francs ($14) for cows. Fresh hides sell for 35 francs ($7) and salt hides for 40 francs ($8). The export tax is 5 francs per hide. Many hides are also exported by the *saladeros* and *mataderos.* One hundred thousand cattle are slaughtered in the former and a large number in the latter. Meat is much more easily exported than formerly on account of the railroads. The increased supply of hides thus produced, together with the abundance of native tanning materials gives promise of great development of the tanning industry in Paraguay. E. A. B.

Syntheses of Depsides, Leichen Substances and Tannins. EMIL FISCHER (Address), *Collegium,* 1914, No. 525, pp. 8-37. Ester anhydrides of the oxyaromatic acids (phenolic carbo-acids) are designated as depsides because of their resemblance to the tannins.

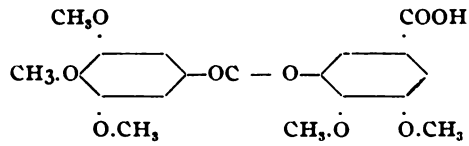
$HO.C_6H_4.CO.O.C_6H_4.CO.O.C_6H_4.COOH$ is an example of a tri-depside. The author has synthesized a large number of depsides by use of his carbomethoxylizing reaction; this consists in treating the phenol carbonic acids with chlorcarbonic methyl ester. The phenol group is easiest attacked when in the m- or p-position to the acid group and several hydroxyls may then react. The o-hydroxyl is not easily affected but the reaction succeeds in presence of dimethyl aniline. Polyphenolic acids may be partially esterified, for instance with gallic acid, the carbomethoxyl group enters a m-hydroxyl. The phenol groups in these compounds may be easily wholly or partially regenerated by treatment with dilute alkali. The acid chlorides of these carbomethoxylized acids are made by action of PCl_5 and crystallize much better than those of the free phenol acids. Further diazo-methan was used as a reagent for complete methylation of all hydroxyl groups. *Didepsides*: The simplest example of one of these syntheses starts with p-oxybenzoic acid; this is coupled with the chloride of its carbomethoxyl derivative:

$$CH_3 - CO_2.O.C_6H_4.COCl + NaO.C_6H_4.COONa =$$
$$NaCl + CH_3 - CO_2.O.C_6H_4.CO.O.C_6H_4.CO_2.Na.$$

Digitized by Google

The free acid from this salt is then de-carbomethoxylized. A list of 27 synthesized didepsides including lecanoric acid (identical with that from archil) is given. A few tri- and tetra-depsides have been prepared. *Tannins*: Gallotannin and allied substances are classed as acyl compounds of sugar with phenol carbonic acids. Strecker (1854) formulated tannin as a compound of 3 mols. gallic acid, 1 mol. glucose. Schiff condensed gallic acid into an anhydride precipitating gelatine which he formulated as $C_{14}H_{10}O_9$, digallic acid and the essential constituent of tannin; later researches proved it not to be identical with tannin.

The views of Nierenstein, Feist and others in recent times concerning the constitution of tannin are not shared by the author. He describes his synthesis of penta-galloyl glucose (abstr. this JOURNAL, 1912 [7], 390). This is probably a mixture of two stereo-isomers. He next attempted the synthesis of Herzig's methylo-tannin. Penta-methyl-m-digallic acid (new)



was prepared by coupling tri-methyl galloyl chloride with mp-dimethyl gallic acid. The product was then condensed with both α- and β-glucose yielding two penta-acyl derivatives of different rotary powers. They are probably both mixtures of two stereo-isomers, and closely resemble a methylotannin prepared from Chinese galls by Herzig's method, but such amorphous substances of high molecular weight cannot be precisely compared. An attempt was made to synthesize tannin itself, starting with m-digallic acid, which was built up by the same general method as the penta-methyl compound. The carbomethoxyl derivative as well as its chloride refused to crystallize and so far have given no definite compounds on condensation with sugar.

These general methods give substances of the highest molecular weight yet synthesized, that of the penta [pentamethyl-m-digalloyl] glucose reaching 2051. By condensing p-iodophenylmaltosazon with tribenzoyl galloyl chloride a definite product of molecular weight 4021 has been attained. W. J. K.

(A very brief abstract of this paper was given on p. 486, Vol. 8.)

Production of Tanning Materials in German Colonies. *Technikum*, 1914, 20-3, 25-7. Germany produces only about one-sixth of the tanning material needed for her own use, oak and fir bark being the chief kinds. Many kinds of barks and extracts are imported from all parts of the world, including mangrove from East Africa, Madagascar, South America and India, mimosa (wattle) from Australia and South Africa, mallet from Australia, myrobalans from India, divi-divi and algarobilla from Central and South America, knoppern from Austria-Hungary and the Danube countries, valonia and trillo from Asia Minor and Greece, que-

Digitized by Google

bracho from South America, chestnut extract from France and Italy, gambier from Sumatra and sumac from Italy. Imports for 1912 total $10,400,000 and exports $2,200,000.

The cultivation of tannin plants is of great importance for the development of the colonies. Hr. Bodenstab has investigated recently the possibilities of culture of tannin plants in German East Africa, especially mangrove, mallet, mimosa, myrobalan, divi-divi and quebracho.

Mangrove.—The low price and high tannin content of mangrove make it especially desirable both for tanning and making extract. It grows extensively in the tropical regions of Africa. In German East Africa the eastern type of mangrove prevails (like that in Asia, Australia, etc.) while in Kamerun the western type grows (like that in America). Reforestation with mangrove is being practiced in German East Africa both for the bark and the valuable wood, and attempts are being made to establish extract works right there for making both liquid and solid extracts, which are of course easier to transport than the bark.

Successful attempts have also been made to decolorize the extract so that it will not make the leather so red. It is a question whether this eastern mangrove, which is richer in tannin than the other, can be raised in Kamerun, although attempts are being made.

Official statistics give the following figures for the export of mangrove bark from German East Africa.

	Weight, tons	Value
1909	3,200	$ 9,279
1910	2,600	25,141
1911	8,600	200,000

Mimosa.—Formerly mimosa came only from Australia, but now it is also grown in large quantities in British South Africa—Natal. The import into Germany is about 24,000 tons of which 20,000 tons come from British South Africa. There is no reason why this product cannot be grown in the German colonies, especially in the mountainous regions of West Usambara and the neighborhood of Kilimandjaro.

The government five years ago provided the colonial industry committee, supported by the Central Union of German Leather Industry with land for experiments in growing mimosa from Natal. It is to be expected that later a good mimosa bark will be produced here and probably also in the highlands of Kamerun where the climate is favorable, so that eventually as much or more can be imported from German colonies as from British South Africa.

Other Acacias.—A great many acacias grow in Africa besides the mimosa. Investigation has, however, shown that the species *suma, spirocarpa, usambarensis,* and *verugera* contain too little tannin to be of use. The *Acacia saligna,* however, contains 28.8 per cent. and experiments must be made with it in German colonies. In German Southwest Africa the *Ganib* (*hynora longicaulis*) is found. It contains about 32 per cent. tannin but has such a high starch content that it cannot be readily leached.

Digitized by Google

Perhaps, however, it could be made into extract, and in any case must not be lost sight of. Mimatschil bark, from the Pithecolobium tree, is found in Saipan, an island in the German South Seas possessions. It contains 28 per cent. tannin, and is therefore destined to be very valuable if it can be produced continuously in large quantities at a low price.

Divi-divi, Gambier, etc.—Experiments are now being carried on in German Southwest Africa to see whether the divi-divi, grown in South America, and so rich in tannin, cannot be raised there. No attempts have been made to raise gambier plants in the colonies but no reason is apparent why this could not be done. Experiments have been made in the culture of mallet bark from Australia, but sufficient time has not elapsed to know results. It is by no means improbable that in a short time Germany will need to import no foreign tanning material if development in her colonies goes on, as it seems likely that it will when the problems of method and transportation are solved. E. A. B.

Salt Stains. *Le Cuir*, VII, 45-6, *Technikum*, 1914, 27-8. A commission has been appointed to study the problems of salt stains, Messrs. Tainturier, Vourloud, Jossier, Luc, Bertrand, Livache, Lindet and A. Martin. This commission plan to try experiments as follows: 1. Fresh hides washed in pure water and salted with sea salt. 2. Fresh hides washed in brine and salted with sea salt. 3. Fresh hides washed with pure water, placed 24 hours in a solution of magnesium chloride of 18° Bé., and salted with sea salt. 4. Fresh hides washed with pure water, placed 24 hours in 18° brine, salted with sea salt. 5. Fresh hides washed in pure water, placed in an 18° solution of magnesium chloride, kept under observation. 6. Fresh hides washed in pure water, salted with sea salt with the addition of 5 per cent. of magnesium chloride. 7. Fresh hides not washed, salted with sea salt with the addition of 5 per cent. magnesium chloride. These experiments are to be started at the beginning of the warm weather; the hides are to be kept under observation during this period, and after being examined by the commission in the fall, started into the tanning process. No. 5 is to be tried at once, on the suggestion of Prof. Bertrand, the hides being kept under constant observation; the object of this being to determine the effect of substituting for ordinary salting the treatment with a solution of magnesium chloride. Professor Bertrand also proposed experiments to test the bad effects attributed to "schlott" (grains found in commercial salts, consisting of sulphate of lime and sulphate of soda in equal parts). One lot is to be salted with sea salt without schlott, one with rock salt without schlott and one with sea salt having grains of schlott specially added. It was suggested that salt makers be asked to add barium chloride to the liquors before the crystallization of the salt, thus precipitating the sulphates and preventing the formation of schlott. L. B.

Digitized by Google

are given: (i) Para-phenol-sulphonic acid is heated for about 24 hours at 120° C. and a pressure of 20 mm. until it gives the maximum precipitation on testing with a dilute solution of glue. The product may be used directly, or it may be purified to a white powder form by neutralizing it with caustic soda, filtering, and evaporating it. (ii) The product obtained by heating phenol gently with concentrated sulphuric acid is heated for 72 hours at a temperature of 140° C. and a pressure of 20 mm. (iii) Ortho-cresol-sulphonic acid is heated at 130° C. and 20 mm. pressure until it gives the maximum precipitation with glue solution. The product is filtered, neutralized with caustic soda and evaporated to dryness. (iv) 1,000 parts of crude cresol-sulphonic acid are heated at about 130° C. and 20 mm. for about 24 hours, and, after cooling to about 80° C. 186 parts of phosphorus trichloride are stirred in at ordinary pressure. The product is taken up with ice and water, allowed to stand, and worked up as in example (iii). (v) 3 parts of crude cresol-sulphonic acid and one of para-phenol-sulphonic acid are heated for 48 hours *in vacuo*. The mixture is cooled and 18 parts of water are added. It is filtered and the filtrate nearly neutralized so that about 5 per cent. of acid remains. The product is cooled in ice and evaporated to dryness. (vi) 225 parts of the sulphonation product of crude cresol are heated with 262½ parts of phosphorus oxychloride for 4 hours at 60° C. The excess of oxychloride is distilled off and the product is washed with hydrochloric acid. In an example of the use of the substances, the product of example (iii) is dissolved in water, with the optional addition of acid, to give 3/5° Bé. The limed and bated skins are hung in this bath and the strength is gradually increased during ten days to 5° Bé. The tannage requires about fourteen days, after which the leather is neutralized, fatted, and dried. Alternatively, drumming or paddling in more concentrated solutions may be employed.

Tanning Material. U. S. Patent No. 1,089,797. OTTO SCHMIDT and JULIUS MÜLLER, Germany; assignors to Badische Anilin & Soda Fabrik. Condensation products from phenol-sulphonic acid, containing sulphur and free from diphenylmethane compounds.

Hide-Working Machine. British Patent No. 24,935. J. STRAITON, Bootl,e Lancashire.

Treating Extracts. British Patent No. 24,982. J. Y. JOHNSON, London. (Badische Anilin & Soda Fabrik.) Difficultly soluble vegetable extracts are rendered soluble by treatment with a condensation product of an aromatic phenol or its sulphonic acid, which product possesses one or more hydroxyl groups and also one or more salt-forming groups. As an example, five hundred parts by weight of quebracho extract are treated with the sodium salt of a product obtained from formaldehyde and cresol-sulphonic acid, dissolved in one hundred parts of water. The thick extract is thereby rendered thin and soluble. The condensation products may also be added to thin extracts before they are concentrated, and in some cases they have a bleaching tendency.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. IX MAY, 1914 No. 5

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1914, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VEITCH, } . . . Past Presidents

OFFICERS, 1913-'14

PRESIDENT—W. K. ALSOP, Ridgway, Pa.

VICE-PRESIDENT—C. W. NORRIS, 80 South Street, New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

LLOYD BALDERSTON, Ridgway, Pa.

C. R. OBERFELL, Harrisonburg, Va.

T. A. FAUST, 323 Academy Street, Newark, N. J.

CHANGE OF ADDRESS.

R. L. Lafferrander, to % M. W. Shepard, Bethel, Conn.

DIED.

Ogden W. Tunison, South Orange, N. J., an associate member of this Association, died in January, 1914.

THE DETERMINATION OF ALKALINE SULPHIDES- II.

By Douglas McCandlish and John Arthur Wilson.

Under the above title (this JOURNAL, 1913, p. 28) we described our experiences titrating sulphide solutions under various conditions, with a N/10 solution of zinc sulphate containing 50

Digitized by Google

grams of ammonium chloride per liter, using sodium nitroprusside as external indicator. We prepared this reagent in accordance with the following description by Blockey and Mehd (*J. S. C. I.*, Vol. XXXI, p. 369):

> "For the estimation of the sulphides in lime liquor, a N/10 solution of zinc sulphate, to which has been added 50 grams per liter of ammonium chloride, is used."

They previously state in the same paper that—

> "Zinc sulphate alone cannot be used to determine the amount of sulphide in a liquor containing lime or caustic alkali, because the zinc is precipitated not only as sulphide but also as hydroxide. If, however, the zinc sulphate solution contains an excess of ammonium chloride, the precipitation of hydroxide is prevented and the only precipitate is, therefore, zinc sulphide, and the ordinary end-point with lead acetate or sodium nitroprusside can be obtained with accuracy."

Using such a solution we obtained inaccurate results, which we published in our former paper.

In the *Collegium* (Feb. 1914, p. 73), Blockey and Mehd state that we incorrectly ascribe the use of this solution to them, because of an ambiguity in the wording of their original paper. They further state that the reagent which was used in their experiments contained ammonia in addition to zinc sulphate and ammonium chloride. We fail to find any mention made of such a reagent in their original paper.

In all the abstracts* of Blockey and Mehd's original paper which we have read, the reagent ascribed to them is the one which we used.

The provisional method of the I. A. L. T. C. for the determination of sulphides in lime liquors (*Collegium*, 1913, p. 73) is as follows:

> "Filter through S. & S. 605 filter-paper; titrate with decinormal zinc sulphate with the addition of ammonium chloride using sodium nitro-prusside as external indicator as

* Journal of the Chemical Society (London), Vol. CII, part 2, p. 600. Chemical Abstracts (American Chemical Society), Vol. VI, No. 15, p. 2190. S. Hirst, Tanner's Year Book (London), 1913, p. 171.

Digitized by Google

described by Blockey and Mehd (*Collegium*, 1912, p. 300)."

In view of the above facts, we cannot accept responsibility for confusing the reagent employed.

In their last paper Blockey and Mehd describe, as the reagent which gives correct results, the following:

> "A N/10 solution of $ZnSO_4$ to which has been added ammonia until the precipitate has redissolved and also 50 grams of ammonium chloride per liter."

We have not found any practical advantage in this solution over the one containing no ammonia, for the determination of sulphides in lime liquors. It might be well to point out in passing that the amount of ammonia required to redissolve the precipitated zinc hydrate is dependent, to some extent, upon the volume of water in which the zinc sulphate is dissolved; the greater the volume of solution, the greater the amount of ammonia required.

In order to put the solution to a fair test, we took a normal set of conditions. The required weight of zinc sulphate (14.35 grams) was dissolved in 250 cubic centimeters of water, 25 cubic centimeters of ammonia (28 per cent. NH_3) were added, followed by 50 grams of ammonium chloride. The solution was then made up to a liter. This reagent was added drop by drop to 25 cubic centimeters of clear, saturated, lime water. A precipitate of zinc hydrate began to form, which gradually increased, but finally redissolved when about 2.5 cubic centimeters of the reagent had been added.

It is therefore obvious that this solution will give inaccurate results for the determination of sulphides in lime liquors, requiring titrations up to 2.5 cubic centimeters for 25 cubic centimeters of the lime liquor, because of the precipitation of zinc as hydrate as well as sulphide. A titration of 2.5 cubic centimeters for 25 cubic centimeters of lime liquor represents 12 pounds of crystallized sodium sulphide (Na_2S $9H_2O$) per 1,000 imperial gallons.

When more than 2.5 cubic centimeters of the reagent had been added to the lime water, the liquor appeared clear again. This clearing was undoubtedly due to the increasing concentration of ammonia in the liquor. It can also be shown that as the amount of ammonia added to the reagent is increased the tendency for

Digitized by Google

any precipitate to form upon addition to lime water decreases. But, as pointed out in our former paper and confirmed by Blockey and Mehd, increasing the concentration of ammonia causes an increasing error, due to the retention of some of the zinc as zinc ammonium ions, which are not precipitated by soluble sulphides.

It is apparent that the method presents many difficulties, even in the titration of pure lime and sulphide solutions, where the conditions are fairly well defined. We are aware of the following variables affecting the end-point, some of which are noted in our previous paper: the concentration of ammonia, the hydroxyl concentration, and the coloration of the precipitated zinc sulphide by the indicator.

With a view to eliminating the difficulties found in the zinc method, we have attempted the determination of sulphides under entirely different conditions. One of the methods we have tried is based upon the following principles:

1. Cupric sulphide is quantitatively insoluble in slightly acid solutions.

2. The depth of color of a solution of cuprammonium sulphate is proportional to the concentration.

A standard solution of cupric sulphate containing sulphuric acid is added to a measured volume of unfiltered lime liquor. The sulphides are all precipitated as cupric sulphide, the alkalies neutralized and some of the dissolved hide substance precipitated. The cupric sulphate and sulphuric acid must necessarily be present in slight excess. Kaolin is added to the liquor which is then well shaken and filtered. To a measured portion of the filtrate is added a slight excess of ammonia, which converts the excess of cupric sulphate into the deeply colored cuprammonium compound. This excess of copper is determined colorimetrically by comparison with standards. If the solution is not perfectly clear after adding ammonia, it must be filtered. But, even with the double filtration, the method is very rapid.

We have encountered difficulties in matching the colors in some cases because of the carbonation of cuprammonium hydroxide. Carbonation appears to turn the color of the solution from blue to green. If the colorimetric method should fail, some

Digitized by Google

other means of determining the copper may be employed. We make no claims for the method, but believe the principle to be capable of successful application.

THE EQUILIBRIUM OF DILUTE HYDROCHLORIC ACID AND GELATIN.*

By Henry Richardson Procter.

In an earlier paper (*Koll.-chem. Beihefte,* 1911, 2, 243; *J. A. L. C. A.,* 1911, 6, 270) it has been shown that when gelatin jelly is immersed in a dilute acid, an equilibrium results which at a given temperature is dependent only on the ionization and concentration of the acid, which determine not merely the volume of liquid absorbed, but the concentration of the anion in the jelly; and more or less empirical formulæ were given connecting these with the concentration of the ionized acid. It was further pointed out that these formulæ were consistent with the view that a hydrolysable and ionizing salt[1] of gelatin was formed, and that the phenomena of swelling were simply dependent on the relation between the osmotic pressure of the ionizing salt and that of the external acid solution.

The object of the present paper is to indicate the precise nature of these relations, and to show that the formulæ there given, with some slight modification, can be fully explained and justified on the ordinary ionization hypothesis. If this is the case, there seems no reason for the assumption of more complicated and less verified theories dependent on surface-tension and other forces, and involving the unproved and rather gratuitous assumption of a two-phased structure of the jelly. The discussion of the present paper has been confined to the single case of gelatin and hydrochloric acid; but the theory proposed is quite general, and if true in the particular case, must also be true (with different constants) of any other acid, and of other amphoteric proteins, so that its bearing, both on colloid chemistry and on physiological theory, is very wide.

* *Transactions* of the Chemical Society (British), Vol. CV, pp. 313-27.

[1] It is most probable that this salt is a "hydrochloride," in the same sense as "aniline hydrochloride," but as other constitutions are possible, it has been thought better to write "gelatin chloride" simply.

Digitized by Google

The theory assumes that the jelly is a molecular network, in which the water, the acid, and the protein are within the sphere of each other's molecular attractions, and therefore homogeneous in the same sense as any other solution; and it discards the Bütschli - vanBemmelen idea of coarse microscopic pores, although it is not denied that such two-phased jellies exist, and can be produced, and that the pores observed by these investigators had a real existence, probably due to the hardening agents with which their jellies were treated.

It has been shown by the author (*loc. cit.*) that when gelatin swollen with water is treated with a strong acid, such as hydrochloric or sulphuric, the swelling becomes much greater than with water alone, but reaches a maximum at a very low concentration of the external acid, subsequently diminishing in a hyperbolic curve, as the concentration of the acid is further increased. This contraction is obviously due to the anion of the acid, since it can be increased to almost complete dehydration by the addition of its neutral salt; but the exact mechanism of the osmotic pressure is not easy to follow, since the jelly is in itself completely permeable both to the acid and its neutral salt, and their ions, and the explanation given in the paper quoted seems an incomplete one.

The fuller statement is that to satisfy the equation[1] of equality of products (Donnan and Harris, T., 1911, 99, 1575; Donnan, *Zeitsch. Elektrochem.*, 1911, 17, 572), the concentration of the free acid contained in the jelly must have a definite relation to that of the ionized anion of the jelly-salt; and as the latter cannot diffuse from the jelly owing to the colloid nature of its cation, the equilibrium can only be reached by the absorption or expulsion of free acid and of water by the jelly. In order to investigate these relations, it is necessary, not merely to deter-

[1] This equation, which states that the product $H^{\cdot} \times Cl'$ must be equal in both phases, is, of course, in accordance with the mass-law, but the actual distribution of $H^{\cdot}$ and Cl' depends on the thermodynamic equation:

$$\delta n\, RT \log H_1/H_2 = \delta n\, RT \log Cl_2/Cl_1$$

given by Donnan and Harris (*Transactions of the Chemical Society*, 1911, 99, 1575) for the analogous case of sodium chloride and Congo red; whence $H_1 \times Cl_1 = H_2 \times Cl_2$. This equation relates to the ionized portions only, and the non-ionized portions, if any, will be related to the ionized according to the ordinary mass-law equation, $a \times b = kc$.

Digitized by Google

mine the total chlorine contained in the jelly, as had been done in the earlier experiments, but to ascertain what were the relative proportions of ionized and of non-ionized chloride and of free acid in the jelly, and it became evident from the mathematical investigation of the equilibrium that the total chlorine and one of these being known, the others could be calculated.

The most obvious way of determining ionic concentrations is by means of concentration-cells, and much time was spent in unsuccessful efforts to solve the problem in this way. The work, however, has not been fruitless, and the causes of failure may be briefly stated. First, it should have been obvious from the outset that the concentration-cell method, marvellously accurate as it is in the determination of the order of quantity of minute ionic concentrations, was quite unfitted to deal with the massive differences of the same order of quantity which were concerned in the present problem. Secondly, it was proved that the apparent ionic concentration of amphoteric colloid solutions, as determined by the concentration cell, was not the actual concentration of the solution or jelly, but that of a non-colloid acid or salt solution with which it would be in equilibrium, since Donnan's "membrane-potential" at a real or virtual surface mathematically equals and compensates any difference of potential between a colloid solution and its equilibrium acid or salt solution. This is obviously a point of fundamental importance with regard to the frequent use of the concentration cell in physiological investigations, and demands more complete proof than space allows here. The author therefore proposes to make this part of his work the subject of another paper; but it may be noted that means were devised for the approximate measurement of the membrane-potential, which, although only of a few millivolts, corresponded with large percentage differences in the present investigation.

Efforts were also made to solve the problem by conductivity measurements, but the results, although of considerable interest, and possibly of importance to the theory of colloid salts, failed to give information either so complete or so accurate as was subsequently obtained by a much simpler and apparently ruder method; and this was also true of a modification of Veley's

Digitized by Google

colorimetric method with methyl-orange, which, within certain limits, gave useful results.

The method finally adopted rests on the fact that the influence of one salt on the ionization of another depends solely on the concentration of their "common" ion. Hydrolysis depends, therefore, on the hydrion concentration only, whilst the mutual ionization of a salt and its acid is influenced only by the "common" anion. If therefore, sodium chloride is added to a jelly containing gelatin chloride and free hydrochloric acid, the ionization is no doubt repressed, but the hydrolysis of the gelatin salt is not affected, and the free acid is expelled with its associated water to almost complete dehydration by the osmotic pressure of the concentrated chlorine ion, and can be titrated in the expelled salt solution. The weight or volume of acid solution retained by the jelly can be easily ascertained, and is so small that even if the assumption that its concentration is the same as that of the solution expelled is not quite accurate, no serious error is introduced by adopting it. The actual method of experiment was as follows: A quantity of carefully purified thin bone-gelatin of known dry weight (usually 1 gram) was soaked in 100 cubic centimeters of acid solution of known concentration in a stoppered bottle for forty-eight hours, a time which was shown to be sufficient for the attainment of practical equilibrium. The contents of the bottle were then poured into a funnel provided with a finely perforated porcelain plate, covered with a clock-glass, and allowed to drain for two hours, the liquid being received in a graduated cylinder. The volume of the liquid, subtracted from 100 cubic centimeters gives the volume of acid absorbed by the gelatin, and this can be further checked, if necessary, by the weight of the drained and swollen gelatin. By titration with alkali hydroxide and phenolphthalein, the strength of the external acid is determined, and from its concentration and volume, the total acid absorbed by the gelatin is calculated. The swollen jelly is now returned to the stoppered bottle, and dry salt added in the approximate quantity necessary to produce a saturated solution. After repeated shaking, and standing for at least twenty-four hours, equilibrium is again established; the gelatin is shrunk to thin, horny plates,

Digitized by Google

and a futher portion of acid liquid can be separated by the draining funnel, containing the whole of the free acid with the exception of that in the small volume of solution (usually about 1.5 cubic centimeter retained in the jelly. If the quantity of solution is determined by volume, it must not be forgotten that a saturated salt solution contains only 94 per cent. of its volume of water, but the effect on volume of the small quantity of acid present may be safely neglected. The acid salt solution is titrated to determine its concentration of acid, and the quantity is calculated to the whole volume of solution absorbed.

We have thus the means of determining (*a*) the free acid unabsorbed, which forms the "external solution" with which the jelly is in equilibrium; (*b*) the free acid absorbed by the jelly; and (*c*) the chlorine, ionized and non-ionized, combined with the jelly base. The sum of *b* and *c* can be further controlled by the titration of the dehydrated jelly with alkali hydroxide, which with phenol phthalein as indicator, completely decomposes the gelatin salt.[1] The following table gives a series of such determinations with varying quantities of acid, and includes the whole of the results in the series of experiments to which they refer, and are more concordant than would be expected from the comparative roughness of the method. Some of the results are given graphically on the curves, to allow the reader to form a judgment of the trustworthiness of the experimental data; but in many cases there is not room to insert the whole.

The lettered columns in Roman type are observations. The numbered columns in italics are calculated from the observations as follows:

$$1 = \frac{c \times e}{d \times 0.94},$$

$$2 = (e + f) - \frac{c \times e}{d \times 0.94},$$

$$3 = \frac{e}{a \times 0.94},$$

$$4 = \frac{(e + f)}{c},$$

$$5 = \frac{b^2 \times 0.94\, d}{e} = \frac{x^2}{[H]},$$

$$6 = (e + f) - (b \times c).$$

[1] In the actual experimental work the *weight* of solution absorbed was taken as that of the volume, the increase of specific gravity by the acid being in most cases negligible as compared with other sources of error; and the total chlorine in the jelly is the sum of the uncorrected titrations of the expelled acid and the residual jelly. The free acid of the jelly as given in column 1 of the table of experimental results is, however, corrected to allow for the portion of solution still retained by the jelly.

Digitized by Google

Concentration of original 100 c.c of acid solution	Concentration of acid after equilibrium = x	Weight of solution absorbed by 1 gram	Volume expelled by salt uncorrected	Mols. acid in solution expelled by salt	Mols. acid in jelly uncorrected	Total acid absorbed by jelly	Mols. corrected HCl in jelly	Mols. corrected Gel Cl in jelly	Concentration of H in jelly	Concentration of total Cl in jelly	Concentration of ionized Cl in jelly	Mols. Cl in jelly in excess of solution
a	b	c	d	e	f	$e+f$	1	2	3	4	5	6
0.300	0.2950	19.98	18.0	4.405	2.222	6.627	*5.202*	*1.425*	*0.2603*	*0.332*	*0.334*	*0.733*
0.250	0.2450	20.22	18.6	3.680	1 991	5.671	*4.255*	*1.416*	*0.2104*	*0.281*	*0.285*	*0.716*
0.200	0.1945	22.10	21.1	3.245	1.750	4.995	*3.615*	*1.380*	*0.1636*	*0.226*	*0.232*	*0.766*
0.200	0.1940	22.68	21.5	3.325	1.770	5.095	*3.731*	*1.364*	*0.1645*	*0.225*	*0.228*	*0.695*
0.200	0.1925	20.59	19.3	2.925	1.785	4.710	*3.320*	*1.390*	*0.1612*	*0.229*	*0.230*	*0.746*
0.175	0.1685	23.48	23.0	2.990	1.705	4.695	*3.247*	*1.448*	*0.1383*	*0.200*	*0.205*	*0.738*
0.150	0.1435	24.24	23.0	2.555	1.620	4.175	*2.865*	*1.310*	*0.1182*	*0.172*	*0.174*	*0.697*
0.150	0.1434	24.00	23.0	2.550	1.605	4.155	*2.830*	*1.325*	*0.1180*	*0.173*	*0.175*	*0.714*
0.125	0.1180	24.36	23.8	2.125	1.490	3.615	*2.314*	*1.310*	*0.0897*	*0.148*	*0.147*	*0.740*
	0.1052	29.75	29.0	2.310	1.490	3.800	*2.521*	*1.279*	*0.0847*	*0.128*	*0.131*	*0.671*
0.100	0.0944	26.38	25.6	1.740	1.445	3.185	*1.907*	*1.278*	*0.0723*	*0.121*	*0.123*	*0.695*
0.100	0.0930	23.09	22.0	1.480	1.427	2.907	*1.652*	*1.255*	*0.0716*	*0.126*	*0.121*	*0.760*
0.075	0.0680	29.12	27.5	1.380	1.310	2.690	*1.555*	*1.135*	*0.0534*	*0.092*	*0.087*	*0.710*
0.075	0.0666	27.85	27.8	1.305	1.340	2.645	*1.391*	*1.254*	*0.0499*	*0.095*	*0.089*	*0.790*
	0.0576	34.01	34.6	1.410	1.270	2.680	*1.474*	*1.206*	*0.0433*	*0.079*	*0.077*	*0.721*
0.050	0.0420	31.07	30.2	0.845	1.255	2.100	*0.925*	*1.175*	*0.0298*	*0.068*	*0.059*	*0.795*
0.050	0.0406	36.42	36.5	1.025	1.200	2.225	*1.088*	*1.137*	*0.0299*	*0.061*	*0.055*	*0.746*
0.025	0.0172	48.13	48.5	0.415	1.090	1.505	*0.438*	*1.067*	*0.0091*	*0.031*	*0.033*	*0.677*
0.025	0.0170	40.44	39.0	0.340	1.155	1.495	*0.375*	*1.120*	*0.0093*	*0.037*	*0.031*	*0 807*
0.020	0.0122	51.72	52.5	0.300	1.100	1.400	*0.314*	*1.086*	*0.0061*	*0.027*	*0.025*	*0.769*
0.015	0.0120	51.89	52.7	0.305	1.115	1.420	*0.320*	*1.100*	*0.0062*	*0.027*	*0.023*	*0.797*
0.015	0.0077	52.20	53.6	0.090	1.065	1.155	*0.093*	*1.062*	*0.0018*	*0.022*	*0.033*	*0.753*
0.015	0.0073	57.91	60.0	0.123	1.035	1.158	*0.126*	*1.032*	*0 0022*	*0.020*	*0.024*	*0.735*
0.010	0.0032	53.68	54.5	0.025	0.880	0.905	*0.026*	*0.879*	*0.0005*	*0.017*	*0.021*	*0.733*
0.010	0.0028	58.43	59.0	0.024	0.825	0.849	*0.025*	*0.824*	*0.0004*	*0.015*	*0.020*	*0.685*
0.010	0.0025	59.90	62.0	0.023	0.855	0.878	*0.024*	*0.854*	*0.0004*	*0.015*	*0.016*	*0.728*
0.008	0.0018	48.70	50.0	0.019	0.735	0.754	*0.020*	*0.734*	*0.0004*	*0.015*	*0.008*	*0.604*
0.006	0.0011	44.11	44.6	0.019	0.590	0.609	*0.020*	*0.589*	*0.0005*	*0.014*	*0.003*	*0.560*

Digitized by Google

It is obvious that from these results two distinct series of curves can be calculated: those of the actual quantity of each associated with 1 gram or 1 mol. of gelatin, and those of relative concentrations of the different constituents of the jelly and its equilibrium acid solution; and these two sets of curves are not necessarily interdependent.

Taking first the question of quantities, the first problem is that of the determination of molecular weight. By this must be understood, not the weight of the associated group of molecules, which, if the molecular network theory be correct, may be co-extensive with the jelly itself; but the smallest weight which could exist in some ideal non-associating solvent, retaining its chemical structure and reactive powers unaltered. It is obvious that the special characteristic of the colloid state is the tendency to form associated groups of molecules, often of quite indefinite size (as in the case of suspension sols), which, osmotically, act as a single molecule or as a single ion. If it were practicable to isolate the pure saturated salt, the equivalent weight would be that combined with one atom of chlorine, and it would only remain to determine the valency of the base. This is, however, impossible, since gelatin is a very weak base, of which the salts hydrolyze readily, and, on account of secondary reactions, it is impossible so to concentrate the acid as to make hydrolysis negligible. All that we can obtain is a curve, of which the limit at infinite concentration is the completely saturated salt, and before this limit can be predicted, the mathematical expression of the curve must be known. For a week monacidic base, such a curve is given by the Ostwald hydrolysis formula, which, as was shown by the author in the earlier paper already quoted (*loc. cit*), is conveniently transformed into the simple expression $y = \frac{x}{x + k}$, where x is the molecular concentration or normality of the equilibrium-acid, k is the ordinary hydrolysis-constant, and y is the proportion of unhydrolyzed salt to the total base present. Such a curve, if the k is small, ascends at first almost vertically, curves sharply as it approaches unity, and thereafter proceeds almost horizontally, reaching unity only when x becomes infinite. If the k be larger, the ascent is more grad-

Digitized by Google

ual, and the curve rounder and more prolonged, so that it may still be far from unity within the limit of experiment, y having obviously a value of 0.5 when $k = x$.

The curve of gelatin chloride plotted from experiment, as will be seen by reference to Fig. 1 rises vertically at first, with all the characteristics of a small k, but after turning sharply, continues to rise throughout the limits of the experiment. Such a curve is that of a diacidic base, or dibasic acid, and is the sum of two curves, one of which is due to the (usually small) k of the first valency, and the other to the larger k of the second. The expression therefore becomes $y = \frac{x}{x + k_1} + \frac{x}{x + k_2}$, and its limit is 2.[1] The experimental curve is plotted for 1 gram of gelatin, whilst the expression is for 1 mol., and must obviously be multiplied by $\frac{1{,}000}{\text{mol. wt.}}$ to make it comparable with experimental results. There are thus three unknowns to be determined, the two k's, and the molecular weight; and, although this might no doubt be done by three simultaneous equations from different points of the curve, I have preferred as more satisfactory, to adopt a method of approximation which apparently is identical in principle with one described by Lundén (*Meddel. K. Vetensk. Nobelinstitut*, 1, No. 11).

Where k_1 is small and k_2 large, the earlier part of the curve is almost entirely dependent on the former, whilst the later part is approximately $1 + \frac{x}{x + k_2}$. If, therefore, the value of the curve at $x = 0.01$ be assumed to be equal to the reciprocal of the molecular weight, and this be subtracted from the value at $x = 0.25$, the remainder, multiplied by the same reciprocal, will be the value due to the second term of the expression, and from these an approximate k_1 and k_2 can be calculated. If these are now employed to correct the first calculations, a closer approximation can be obtained; and this can be repeated until the results are

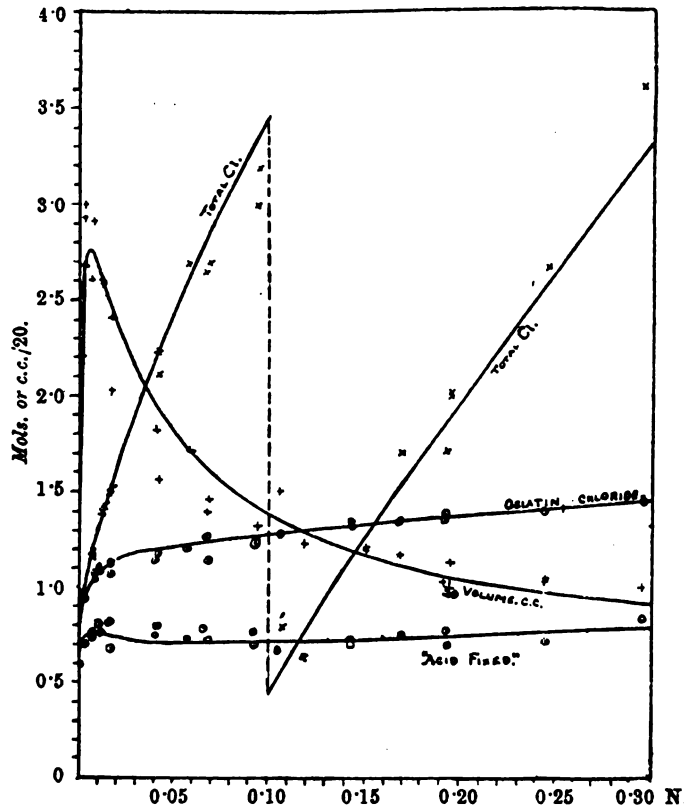
[1] The curve of non-hydrolyzed gelatin given in a previous paper was calculated on purely theoretical grounds and on the assumption that gelatin was monacid, and the k then adopted of 0.005 was obviously a compromise between k_1 and k_2.

Digitized by Google

within the limits of experimental error. For each single term, $k = \frac{x}{y} - x$. With any approximate molecular weight values for k_1 and k_2 can be calculated which will give a curve agreeing

FIG. 1.

Curves of quantity: 1 gram.



with the experimental at the two points taken, but unless the molecular weight is very nearly correct, the value of y will be noticeably wrong at a third point, which is most advantageously taken near that of maximum curvature.

Since the molecular weight must be such as will give whole numbers of atoms in accordance with ultimate analysis, it be-

Digitized by Google

comes easy to decide on the only possible weight within the limits of experimental error, and a "rational" formula is obtained.

The experimental curve in the present case is very accurately represented by $\frac{x}{+ 0.0013} + \frac{x}{x + 1.05} \cdot \frac{1,000}{839}$, and to this the curve in Fig. 1 has been calculated. This results in a probable "rational" formula for gelatin of $C_{35}H_{57}O_{13}N_{11}$, with a molecular weight of 839, which agrees with Schützenberger's own determinations quite as well as his generally accepted formula, $C_{76}H_{124}O_{29}N_{24}$, but is slightly higher in nitrogen than the average of published analyses, as is shown by the following table. It is probable that the difference may be accounted for by the extreme difficulty of completely drying gelatin without decomposition. The hydrogen is, of course, the most doubtful number.

Formulæ		Analyses		
Procter $C_{35}H_{57}O_{13}N_{11}$	Schützenberger $C_{76}H_{124}O_{29}N_{24}$	Schützenberger	Mulder	Chittenden and Solly
C 50.06	49.7	50.0	50.1	49.4
H 6.79	6.8	6.7	6.6	6.8
O 24.79	25.2	25.0	25.0	25.1
N 18.36	18.3	18.3	18.3	18.0

It may be noted that Paal obtained a molecular weight of about 900 from freezing- and boiling-point methods (*Ber.*, 1892, 25, 1202).

It must not, however, be assumed that the molecular weight of gelatin, from the physical point of view, is necessarily so comparatively small. The weight calculated from the previous experiments is merely that of the smallest quantity which can act as a chemical individual, and it is not incompatible with the association of the colloid molecules in any way which does not affect their chemical combining powers; and, if the view of a molecular network is correct, the whole jelly may be regarded in a physical sense as one enormous colloidal molecule dissociating a number of chlorine ions; whilst it is impossible to say what degree of association may still exist after liquefaction.

Since the hydrolysis-constant of a salt of a weak base is the ionization constant of water divided by that of the base, we can calculate the two basic constants of gelatin as concerned in the reaction, although it may be probable that the two affinities are

Digitized by Google

in themselves equal, and that the second only takes its lower value because of the previous saturation of the first.

Since $k_w = 0.6 \times 10^{-14}$ and $k_1 = 1.3 \times 10^{-3}$, $k_{h_1} = \frac{0.6 \times 10^{-14}}{1.3 \times 10^{-3}}$ $= 0.5 \times 10^{-11}$, and $k_{h_2} = \frac{0.6 \times 10^{-14}}{1.05} = 0.6 \times 10^{-14}$. Lundén (*loc. cit.*) gives for leucine $k_a = 1.8 \times 10^{-10}$, and $k_b = 2.3 \times 10^{-12}$, and for glycine (aminoacetic acid) one of the principal constituents of the gelatin molecule, very similar figures, so that there is no inherent improbability in those calculated.

Turning from the question of quantities to that of concentrations, if we represent on a curve-diagram the hydrogen-ion concentrations by the abscissæ and those of the chlorine-ion by ordinates, the common concentrations of the external acid x, in which these are equal, will intersect on a line passing through the origin at an angle of 45°, and this will be the axis of a series of right-angled hyperbolas, corresponding with the different values of x, and of which x^2 will be the generating square; and on which, for each value of x, all possible solutions of the equation $x^2 = H \times Cl$ will lie, and if the concentration of one of these constituents is given, the equilibrium will be definitely determined. At any such point, the hydrogen and chlorine ordinates will enclose a rectangle equal in area to x^2, the chlorine being necessarily the greater from the ionization of the gelatin chloride.

It is obvious that on the concentration of this ionized chloride the whole equilibrium depends, and if its relation to x can be determined, the problem is definitely solved. An experimental solution is given by the determination of the concentration of the free acid of the jelly, which is equal to its hydrogen abscissae. As the jelly is completely permeable to the ions of the external acid, it must be in equilibrium with it both osmotically and thermodynamically, that is, both the total concentration of ions and the product of the hydrogen and chlorine ions must be the same in each case, or any difference which exists between the two must be compensated by an electric potential at the interface. There is no evidence, experimental or theoretical, that the colloid gelatin ion exerts any osmotic pressure, and, as an associated

Digitized by Google

network, it should, theoretically, only act as a single molecule; but since the two sides of a rectangle are necessarily greater than those of a square of equal area, some surface-potential must exist, opposed in sign to that shown by Donnan (*loc. cit.*) to be caused by the unequal concentration of the hydrogen and chlorine ions. Since the ionized chlorine is confined to the jelly by the attraction of its non-diffusible colloid ion, the adjustment of equilibrium between the jelly and the external acid can only take place by the passage inwards or outwards of hydrochloric acid and water, and if we suppose the jelly divided into separate volumes, each containing one of the constituents at the common osmotic pressure, that of the acid will be of the same concentration as the external acid x, and will have an osmotic pressure of $2x$, since both hydrogen ion and chlorine ion are of x concentration, and the ionized chlorine, to be at the same osmotic pressure, must also have a concentration of $2x$, since the chlorine ion of the acid cannot be expelled without its attendant hydrogen ion.

Thus the x^2 of the external acid is in osmotic equilibrium with the $2x$ of the jelly, and if we plot the concentration of the external acid as x, we must also plot the osmotic concentration as $\sqrt{2x}$ to maintain the same relation. Experiment shows that, measured in terms of x, the concentration of the ionized chloride is approximately $\sqrt{2x}$, but is more accurately expressed by $\sqrt{2x + 0.02}$, the explanation of the small correction being discussed later.

Calling the concentration of the ionized gelatin chloride Cl_x, the concentration of hydrogen ion in the jelly is algebraically $\frac{-Cl_x + \sqrt{Cl_x^2 + 4x^2}}{2}$ and that of the expelled acid

$$x + \frac{Cl_x - \sqrt{Cl_x^2 + 4x^2}}{2};$$

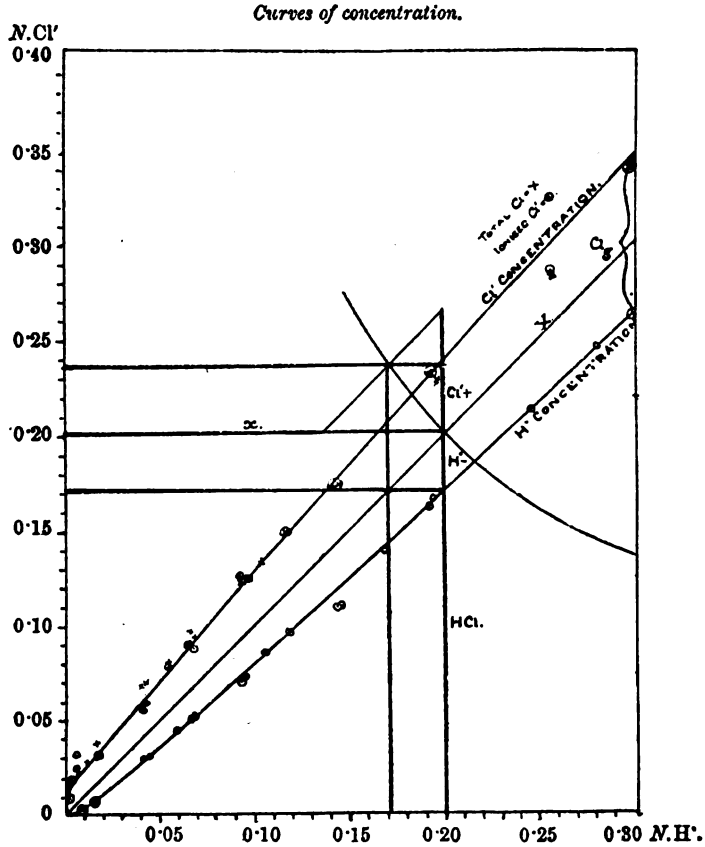
but, graphically, all the concentrations are given by a simple construction, the proof of which is obvious. If the Cl′ ordinate of x be produced vertically to an additional length of Cl'_x, and a line be drawn through this point parallel with the axis of the hyperbola (that is, at 45°), it will cut the hyperbola at the common point of intersection of the H· and Cl′ ordinates of the jelly, the H· ordinate of which, if produced, will cut the x ver-

Digitized by Google

tical at the total Cl′ concentration, and a horizontal line through the point where the Cl′ ordinate of the jelly cuts the axis of the parabola will cut the x vertical at the hydrogen-chloride concentration of the jelly, whilst the difference between this and x will be the acid expelled. If continuous curves are drawn through

FIG. 2.

Curves of concentration.



these points for the different values of x, they will divide the diagram into regions of free hydrogen chloride or hydrogen-ion concentration, and of ionized chloride, respectively, below and above the straight-line axis of x. Experimentally, the concentration of the ionized chlorine is obtained by dividing x^2 by the concentration of free acid in the jelly, and that of the total chlor-

Digitized by Google

ine by direct titration. Both are plotted in Fig. 2, but the ionized is marked O and the total $\times$. It will be seen that they practically coincide, and it may be concluded that the gelatin salt is almost wholly ionized, or, at least, to an extent comparable with hydrogen chloride, for the incomplete ionization of which no allowance has been made.

With regard to the correction, approximately 0.02, added to $2x$ under the square-root sign, it may be noted that, putting $x = 0$, a value of chlorine-ion concentration still remains equal to $\sqrt{0.02}$. This ionization of chlorine in absence of an appreciable hydrogen-ion concentration is also confirmed by experiment, a measurable chlorine-concentration being reached before any free acid is shown either by indicators like methyl-orange, or by the hydrogen concentration cell. The probable explanation is that as gelatin is amphoteric, and, to some extent, ionizes both $H^{\cdot}$ and OH' in the neutral state, a small amount of neutral chloride can be formed in absence of any other free acid than its own; or, perhaps, in other words, that it must be brought to a neutral condition as compared with water before any hydrolytic production of hydrogen chloride can take place. This is in accordance with experiments quoted by Pauli (*Koll.-Zeitsch.*, 1913, 12, 222), which prove that in neutral solution, gelatin and other proteins wander to the positive pole in electrophoresis, and that a small amount of acid is necessary to bring them to a neutral condition in which they are unaffected by the current, whilst, with further additions of acid, their basic character preponderates, and they wander to the negative pole (probably as basic ions). The correction may thus be regarded as simply indicating the amount of hydrochloric acid required before neutrality is reached.

It is obvious that, except for this small correction, the concentrations are all purely mathematical functions of x, and therefore independent of the chemical properties of the protein, and applicable to all substances capable of similar equilibria. If the temperature is raised so that the jelly melts, it can be shown that equilibrium still exists, although actual measurement is complicated by the necessity of a membrane, and the much longer time required to attain equilibrium than with the thin

Digitized by Google

sheets of the present experiments; but, in the case of gelatin, neither concentration cells, conductivity, nor the experiments of G. S. Walpole on refractive index (*Koll.-Zeitsch.*, 1913, 13, 241) show any break in the curves at the melting point, and, in all probability, the degree of association is still very large. Since such associated groups of ions must still be in equilibrium with their surrounding solution, they must also be associated with acid and water in the terms of the jelly equilibrium, and the suggestion is obvious that, whilst the true equilibrium-jelly is a homogeneous molecular solution, the apparent aqueous solution is really a two-phased structure of associated colloid systems, surrounded by their equilibrium liquid. The same may probably be true of jellies made up with arbitrary quantities of water and acid, and may serve to explain some of the results of earlier investigators. Certainly, electrometric experiments made with such jellies, both by conductivity and by the concentration cell, gave somewhat abnormal results; and it is clear that unless by chance the exact equilibrium mixture has been made, they must be in unstable equilibrium, and must tend to separate into equilibrium-jelly and its corresponding acid, possibly developing the Bütschli sponge-structure.

In this connection, it is well to refer to the work of Pauli (*loc. cit.*) on the viscosity of acid protein solutions, in which he obtained curves identical in type with the swelling curve of acid gelatin, which probably can be explained by the varying quantities of water and acid associated with the gelatin molecules.

It was shown in the earlier paper (*loc. cit.*) that the volume of swelling was nearly proportional to $\frac{x}{x+k} + \sqrt{x}$ or $\frac{\sqrt{x}}{x+k}$, or to the theoretical quantity of non-hydrolyzed gelatin divided by $\sqrt{x}$. Obviously, if the *quantity* of ionized chloride at any point be divided by the corresponding *concentration* of the ionized Cl′, the quotient will be the volume of the jelly, and it is found that by dividing the calculated quantity of non-hydrolyzed chloride which, it has been shown, is almost wholly ionized, by $\sqrt{2x + 0.02}$, a curve is obtained which agrees very closely with the smoothed curve of observed volumes, both in type and quantity. It is worthy of note that the above calculation takes

Digitized by Google

no account of any solid rigidity or elasticity of the jelly, and it may therefore be presumed that these have no existence apart from the osmotic pressures of the jelly, or, at least, that they are of negligible amount.

Finally, a large number of determinations were given in the earlier paper of what was called "acid fixed;" that is, of the excess of acid in the jelly over that contained in an equal volume of the external solution. This is a well-defined quantity, rising rapidly with the concentration of the external acid to about 0.8 milligram-molecule for 1 gram of dry gelatin, forming a slight maximum at about $x = 0.015$ and a still less marked minimum at about $x = 0.15$, and again increasing, but only very slowly. The value is easily and accurately obtained by titration of the melted jelly and of its equilibrium acid, but the curve is peculiar; and, at the time, was incapable of definite explanation. It is now obviously the quantity of gelatin chloride less that of the free acid expelled. Calling Q the value of the quantity of non-hydrolyzed gelatin chloride, c the concentration of the ionized chloride, and a that of the expelled acid, this is given by the (somewhat simplified) expression $Q\frac{c-a}{c}$. This accurately reproduces the peculiarities of the experimental curve, but is very slightly too low in actual quantity, presumably because the theoretical expression assumes total ionization of the gelatin salt, and the consequent expulsion of a slightly larger quantity of free acid than actually takes place.

All the curves described are plotted in Figs. 1 and 2, together with the experimental results (so far as space allows), and the corresponding algebraical expressions are annexed; and to facilitate experimental checking, the numerical calculated values for a number of values of x are also given in the following table.

The following are the formulæ used in calculation; the letters refer to the corresponding columns.

$$a = \left(\frac{x}{x + 0.0013} + \frac{x}{x + 1.05}\right) \cdot \frac{1{,}000}{839}$$

$$b = a + c$$

$$c = \frac{a \times f}{g}$$

Digitized by Google

$$d = b - ex$$

$$e = \frac{a}{g}$$

$$f = \frac{-\mathrm{Cl}_g + \sqrt{\mathrm{Cl}_g^2 + 4x^2}}{2}$$

$$g = \mathrm{Cl}_x = \sqrt{2x + 0.02}$$

$$h = f + g = \frac{x^2}{f}$$

$$i = x - f$$

CALCULATED MATHEMATICAL CURVES FOR 1 GRAM OF GELATIN.

Normality of eq. acid.	Quantity unhydrolyzed gelatin chloride.	Quantity total Cl of jelly.	Quantity free acid HCl of jelly.	Quantity excess of Cl in jelly over eq. vol. solution.	Volume of jelly.	Concentration H'.	Concentration Cl_g'.	Concentration total Cl'.	Concentration at H' expelled.
x	a	b	c	d	e	f	g	h	i
0.001	0.520	0.522	0.002	0.481	35.0	0.00007	0.0149	0.0149	0.0009
0.002	0.725	0.737	0.012	0.615	46.8	0.00025	0.0155	0.0157	0.0018
0.005	0.952	1.023	0.071	0.750	54.7	0.0013	0.0174	0.0187	0.0037
0.010	1.066	1.285	0.219	0.754	53.3	c.0041	0.0200	0.0241	0.0058
0.015	1.114	1.494	0.380	0.747	49.8	0.0075	0.0223	0.0298	0.0075
0.02	1.142	1.664	0.522	0.732	46.6	0.0112	0.0245	0.0357	0.0088
0.03	1.176	1.965	0.789	0.720	41.6	0.0190	0.0283	0.0473	0.0109
0.05	1.216	2.467	1.251	0.710	35.1	0.0356	0.0346	0.0702	0.0144
0.10	1.279	3.440	2.161	0.714	27.3	0.0793	0.0469	0.1262	0.0207
0.15	1.330	4.253	2.923	0.718	23.5	0.1244	0.0566	0.1810	0.0256
0.20	1.375	4.987	3.612	0.743	21.2	0.1702	0.0648	0.2350	0.0298
0.25	1.415	5.662	4.247	0.758	19.6	0.2165	0.0721	0.2886	0.0335
0.30	1.452	6.318	4.866	0.773	18.4	0.2632	0.0787	0.3419	0.0368

The dehydrating effect of salts having a common ion with the acid has not been dealt with experimentally in the present paper, since it is obvious that if the anion of the acid diminishes swelling, by increasing osmotic pressure and concentration, additional quantities of the same ion introduced as neutral salt must have the same effect. Even numerically, so long as the salt solutions are dilute, it is probably sufficient to take account of the common ion only, using the same mathematical formulæ as with the acid alone, but with more concentrated solutions, the effect on ionization at least must be considered, and we can no longer assume that the colloidal salt is totally ionized.

Digitized by Google

It was shown in the earlier paper that when a salt with no common ion is introduced, as, for instance, sodium chloride into a solution of gelatin formate, a quadruple equilibrium is produced, in which each anion is in equilibrium with its own gelatin salt. This has been shown rather strikingly by a recent experiment with the substances just named, in which the gelatin was shown by analysis to have combined with as much as 3 per cent. of hydrochloric acid derived from the sodium chloride. Similarly, in presence of large excess of sodium formate, hydrochloric would be replaced by formic in the gelatin salt, and this sort of reaction is not without bearing on some physiological problems.

The question whether the action of neutral salt solutions on gelatin falls under the same theory still demands further study. It was shown in the previous paper (*loc. cit.*) that sodium chloride was absorbed by gelatin from neutral solution with increased swelling, but was replaced and expelled by hydrochloric acid, in presence of which the absorption of salt was negative. Neutral salts may combine with amphoteric proteins, either by the anion becoming attached to the amino- and the cation to the carboxy-group, or the whole salt may be attached to the amino-group, as hydrogen chloride is to organic bases, by the nitrogen becoming quinquevalent; and the probable structure of the protein salt must be left to more purely organic chemists to decide, since either would fulfil the requirements of the present theory.

Conclusions.—The swelling of gelatin in dilute acid solutions depends on the osmotic pressures and equality of products of a diacid ionizable salt or gelatin as a base, and of the external acid with which it is in equilibrium; and the ionization-constants and molecular weight being known, all the other quantities are determined. The method is general and applicable to other proteins and other acids.

The ionic concentrations in the jelly are all mathematical functions of that of the equilibrium acid, and independent of the chemical nature of the gelatin or other protein.

While gelatin jelly in equilibrium with an acid is believed to be a molecular solution, jellies and colloid solutions, in which

Digitized by Google

the conditions of equilibrium are not fulfilled, are probably two-phased structures, and may exhibit the pores described by Bütschli and van Bemmelen.

PROCTER INTERNATIONAL RESEARCH LABORATORY,
UNIVERSITY OF LEEDS.

THE COLOR MEASUREMENT OF EXTRACTS.*

By Henry R. Procter.

There are two objects which may be served by the color-measurement of extracts: Firstly the tanner desires to know what color a given extract will produce on his leather; and secondly in making a contract with the extract manufacturer he desires to bind him by a precise statement of the color to be supplied. Curious as it may seem, it must be admitted that in the present state of our knowledge, neither of these problems is easy of solution, and that different methods must be employed for each.

Imperfect as the method of tanning tests may be, it is probably the best known solution of the first requirement, but from the variation in color caused by slight differences in proceedure and hide material and the uncertainty that any tanning test can be exactly reproduced, it is far from satisfactory as a basis of contract. To obtain fairly comparable results every care must be taken to use exactly the same skin material, and to agitate it for the same time, in liquors of the same strength, acidity and temperature.

The International Association has a prescription in which sheep-grain preserved and delimed in a boro-phenol solution is used as the skin, and the drumming is in very weak liquors, this gives four comparative results, but is certainly capable of improvement. For sole leather tanners, split-hide is probably a better, if more costly material and this split or shaved calf skins give also good and even results. It is not certain that boro-phenol is the best preservative; and Jones' formic mercury treatment followed by salting seems worth trying.

The liquors should for comparison be made direct from the extracts, but much useful information may be obtained for the

* *Shoe and Leather Reporter*, March 19, 1914.

Digitized by Google

tanner by trying the various possible mixtures and additions, acids, bisulphates, alums, magnesium sulphates, etc., and if the skin is sufficiently thick to be incompletely tanned in a given time, say two hours, some information may be gained as to rapidity of penetration.

The International Association prescribes ¼ per cent. solution of tanning matter as estimated by analysis, raised to ½ per cent. as the tannage progresses, but probably a more practical method would be to commence with, say 200 cubic centimeters of plain water and to dissolve in 200 cubic centimeters a quantity of extract about double that required for tannage or even more, and add this solution, say 20 cubic centimeters at a time, every five minutes till the whole is given, and then carry on the tannage to the end of two hours; or whatever time is fixed. The process is usually most conveniently carried out in a glass jar of sufficient size, rotated in a shaking machine.

When the tannage is complete, there yet remains the question of drying. The sample may or may not be rinsed in water, but is generally pressed or slicked to facilitate drying, and nailed out. It should certainly be dried rapidly in the dark, or at least protected from strong light, but the temperature and whether the leather should be lightly oiled, are points deserving discussion. Oiling and cold drying certainly give the brighter results, but drying unoiled and at higher temperature is the severer test for the extract.

Though several substitutes for skins have been proposed, such as white broad-cloth, and gelatinized cotton cloth, which possibly give more uniform results, these are not identical with actual tannage, and are hardly so much more regular as to compensate for the general information gained by the use of actual skin material, since probably the process can never be made sufficiently accurate to serve satisfactorily as a basis of contract.

For this purpose there is much to be said for the direct optical measurement of the color of the extract solution itself, but this, though more easily and accurately repeated than the tanning test, is not without its difficulties. In England much use is made of the Lorrbond tintometer, which registers the color in terms of graduated colored glasses, but the matching is difficult and af-

Digitized by Google

fected by the light and the observer, and the results are not easily compared, an extract solution of double strength and color requiring less than a double value of glasses.

This latter difficulty is overcome by a method of the writer's, in which a uniform standard of glasses (of 10 units of color) is used, and the thickness of extract solution required to match it is measured. But the experiments of Mr. G. A. Kerr of Lynchburg, Va., have shown that recent glasses issued by the Tintometer Company are not strictly comparable with earlier issues, and are therefore useless, as a standard. To get over this difficulty, the writer is trying to devise a method in which permanent chemical solutions of known compositions are substituted for glasses, and if he succeeds, the results will be communicated without delay to the readers of the *Shoe and Leather Reporter.*

It must always be remembered that though the optical color of any one make of extract is fairly proportionate to that which it will produce on leather, it is never satisfactory for the comparison of two entirely different makes, since the effect on leather depends not merely on the visible colors, but on the special tannins which they may contain.

SOME RECENT ADVANCES IN THE CHEMISTRY OF THE TANNINS.*

By M. Nierenstein.

The chemistry of the tannins has often been called "the Central Africa of Chemistry," and though this part of the "Black Continent" has been explored many times in recent years, the expeditions have been so far merely trips into the borderland, and sometimes absolutely misleading results have been obtained from such reconnaissances, which have often been headed by the author of this article. As one who has been engaged in research for more than ten years on this fascinating subject, I venture to say that our present knowledge of the tannins is very unsatisfactory, and often highly hypothetical. However, some important facts have been elucidated in recent years by the investigations of Emil

* *Leather World*, Vol. VI, p. 1-88, March 12, 1914.

Digitized by Google

Fischer, M. Nierenstein, J. Herzig, K. Feist, E. Stiasny, and their co-workers.

Before discussing the points gained by these workers, I must congratulate those who are interested in this work on having enlisted the interest and sympathies of such an eminent chemist as Emil Fischer, whose genius has brought light into some of the most obscure questions in chemistry, such as the constitutions of the sugars, the proteins and the uric acid group, and who may also in the future show us the way in this dark corner of the science.

The chemistry of the "blooms" in tannins and the processes of their formation have been very satisfactorily worked out. It has been shown that nearly all the "blooms" are ellagic acid, a product having a fully established constitution, which has been synthesized in recent years. With regard to the formation of the "blooms," we know that they can be formed:—

(1) By oxidation from the tannic acid nucleus.

(2) By hydrolysis of the ellagic acid glucosides, and

(3) By hydrolysis of ellagitannic acid-like substances into ellagic and gallic acids.

This work has been carried out by my co-workers and myself, who have succeeded also in synthesizing tannins which consist of ellagic and gallic acids. These products are crystalline substances which have the characteristic reactions of tannins, *viz.*, they are precipitated by gelatine and quantitatively absorbed by hide powder; when dissolved in water and allowed to stand, they yield "bloom."

Those engaged in tanning will know that while Knoppern galls do not yield "bloom" when extracted with boiling water, a cold or slightly warm extract produces it in abundance. This behavior was at first difficult to explain. However, some unpublished investigations of the author furnished the missing link, and have shown that the formation of ellagic acid is due to an enzyme. This enzyme, which is killed on boiling, splits the knoppern tannic acid into a product luteoic acid, which readily yields ellagic acid or "bloom."

The author's investigations have shown luteoic acid to be an intermediate oxidation product of tannic and ellagic acids, and

Digitized by Google

that it exists also in myrobalans as a glucoside. Thus we have to add to our list of processes by which the "bloom" is formed, the fourth possibility, *viz.*, its formation by enzyme action on a complex luteoic acid nucleus.

Much work has accumulated round gallo-tannic acid, the tannin of the galls. As, however, this tannin is of no technical importance to the tanner, it need have no more than a mere mention.

The "red" producing tannins, such as quebracho, hemlock, and others, have also been investigated, and a number of points elucidated which explain the formation of the phlobaphenes. As far as our present knowledge extends, the "reds" have a constitution very similar to that of rufigallic acid. Work on this point is in progress in the bio-chemical laboratory of Bristol University, and if the fact is confirmed more fully and shown to be of general application to the reds, it should be of technical importance, as in time it may lead to methods which would tend to lighten the color of dark leather.

Here I should perhaps refer to some work done in the above-mentioned laboratory on electrical tannage. This work has shown that an alternating current does not accelerate the tanning process, while a direct current, on the other hand, accelerates the tannage of hides, but at the same time decomposes the tannins and converts them into non-tannins. This must spell failure to electrical tannage.

Attempts to synthesize tannins have also been made, and here may be mentioned the galloylellagic acids of Nierenstein, the depsides (the name derived from the Greek verb "to tan") of Fischer, and the syntans of Stiasny. The first two are of no technical importance.

Of far greater importance are the Syntans, to which belong the technically known "neradols." These are condensation products of sulphonated phenols with formaldehyde. Professor Stiasny has utilized most ingeniously in their preparation an old discovery of Baeyer (1870), who noticed that pyrogallol forms a tannin-like substance when condensed with formaldehyde.

Digitized by Google

TANNING WITH ARTIFICIAL PRODUCTS.*

By Professor E. Stiasny.

The development of Leather Industries can be traced back to two causes, *viz.*:—

1. The improvement of the methods of applying well-known tanning agents.

2. The discovery of new tanning agents.

The latter way undoubtedly opens more possibilities, because a new tanning material will surely lead to a leather having entirely new properties. In this connection we may mention the invention of chrome tannage, the discovery of the tanning properties of formaldehyde, and of a few other inorganic and organic substance, the tanning effect of which is not utilized as yet on a commercial scale (cerium and bismuth salts, halogens, peat, etc., may be quoted as examples). Any new vegetable tanning material may also be regarded as such a new tanning agent, although the novelty in introducing such a material is not so striking and so interesting as in the case of the above substances.

The tanning agent of which I will give a short account in this paper differs from the above named materials, in so far as it is not a product found in nature, like vegetable tannins, nor is it an inorganic tannin, nor a simple organic body like formaldehyde. In fact it is an artificial organic substance, made by synthesis in a way similar to the methods applied for making aniline dyes.

This condensation product which is formed by the action of formaldehyde on sulphonated phenols belongs to a new class of organic substances called by the author syntans. After further suitable treatment it is brought into the market under the name of Neradol D, and the Badische Anilin & Soda Fabrik are the makers of this first synthetic tannin for techincal use.

It is about two years since the first tanning trials were made with this material on a commercial scale, and there is a great variety of applications known now which offer distinct advantages if compared with the other methods of tanning.

Before entering into the description of the technical application of this synthetic tannin, a few words must be said on its appearance and properties.

* *Shoe and Leather Reporter*, April 16, 1914.

Digitized by Google

Neradol D is a thick liquid extract, similar in appearance to vegetable tannin extract, but brighter in color and much more easily soluble in water. The solution (there are no insolubles left even if cold water is used) is semi-colloidal in character, and gives a deep blue coloration with ferric salts. A precipitate is given on the addition of gelatine, lead salts, aniline hydrochloride and some basic dyes. The color of the leather obtained is white and other characteristic features are: The toughness of the fiber, the kindness and smoothness of the grain, and the property of carrying more grease than leather tanned with any other material.

In dealing with the practical application of this artificial tannin, only general remarks can be made, and the reader is referred to the Badische Company as regards detailed descriptions for special purposes Besides, every intelligent tanner will soon find out such a method of using Neradol D as will suit him best.

Neradol D tannage, like every other tannage, may be given alone or in combination with other tannages, and it is an important feature of this artificial tannin which distinguishes it from so many pseudo-tannins of late, that a very good commercial leather can be produced without the addition of, or combination with, any other materials. The hides or skins after the ordinary preliminary treatment—complete deliming is essential—are simply suspended, paddled or drummed in a solution of Neradol D until a cut shows complete penetration. This indication is not as easily observed as with vegetable or chrome tannage, as Neradol leather is white, but by moistening a fresh cut with a 10 per cent. solution of iron alum, the tanned portions are instantly stained blue, while any untanned middle layer remains white.

Tannage with Neradol D alone is of special interest for sheep and lamb skins, skivers and other light skins; pickled skins (or hides) may also be tanned in this way, and the tannage is still more rapid in this case; in fact the leather turned out with pickled skins has some advantages over the leather from unpickled skins.

It is worth mentioning that no addition of salt to the Neradol D liquor is necessary, and that no swelling takes place even if the goods are brought into the tan liquor directly from the pickle

Digitized by Google

(should a glassy layer be observed in the skins during tannage, a short treatment with salt solution will always remove it).

In the further treatment of Neradol D tanned skins no alkaline fat liquor must be used, as the alkali has a stripping effect on Neradol D tannage. Sulphonated oils mixed with moellon or other emulsions of neutral or slightly acid character may be used.

Dyeing is easiest done with acid aniline dyes, but there are also some basic dyes which can be used without previous mordanting with sumac, gambier or fustic, etc.

As regards combination tannages, a great variety of valuable applications of Neradol D have been found out, but only a few of them can be mentioned here. The most important is the combination of Neradol D and vegetable tannage.

There are several ways of combining these two tannages, *viz.*:—

1. Giving a preliminary Neradol D treatment and then the vegetable tannage.

2. Mixing Neradol D with the vegetable tan liquors, and—

3. Giving a Neradol D treatment on the top of the vegetable tannage.

Of course all these three ways of operating (or two of them) may be combined.

The preliminary tannage with Neradol D has the advantage of tanning the grain a white color, and subsequent vegetable tannage will never cause so dark a color as that obtained without a preliminary treatment.

Moreover, the softness of the Neradol D grain is a safeguard against drawn grain, and the softness remains throughout the vegetable tannage, even if stronger and more astringent tan liquors are used than in ordinary methods.

A further important point is the great hastening effect of such a preliminary treatment on the subsequent vegetable tannage. This point is of practical importance in heavy leather tanning, and, in carrying out this method, the hides are best taken from the second or third suspender—in fact, whenever a complete deliming is reached—and suspended for 24 to 48 hours in a Neradol D solution of such strength that the barkometer reading is slightly less than that of the last vegetable tan liquor. This treatment may be repeated at a later stage of vegetable tanning. From the

Digitized by Google

Neradol D bath the hides may be brought into vegetable tan liquors of distinctly higher strength, and a more rapid increase in barkometer readings with less pits is permissible.

In the acid hemlock or acid oak bark tannage, the Neradol D treatment is most suitable after the desired degree of swelling is reached, as the Neradol D bath will fix this swelling, and have a very valuable effect on color and toughness of the grain. This latter property forms a characteristic feature of all leathers treated with Neradol D before or during the vegetable process.

The addition of Neradol D to the vegetable tan liquors (second method) is especially suitable for belting and harness leather, also for lighter leathers (for instance sumac tannage) and for the drum tannage of any kind of leather. In this latter case not only is the speed of the tannage increased and the color of the leather brightened, but also insoluble parts of the vegetable tanning extracts are solubilized as such a solubilizing effect is one of the general properties of Neradol D. In the ordinary pit tannage of sole leather, Neradol D should only be added to a limited extent to the vegetable tan liquors (not exceeding 5 per cent. on the pelt weight) as larger amounts would tend to produce softness of the leather.

The third method, *viz.*:—using Neradol D on the top of vegetable tannage has a considerable practical importance; completely tanned leathers are bleached by such a treatment, and this bleaching effect is accompanied by re-tannage. The effect is most striking in the case of mangrove tannage and the process is carried out in suspenders or handlers with Neradol D solution of 30 to 40° Bark. in the case of upper leathers. Light leathers are drummed or paddled with a 3 to 5 per cent. solution of Neradol D, while heavy leathers are best brushed with a 40° Bark. liquor.

A Neradol D treatment can also be given to incompletely vegetable tanned goods, and very good results have been obtained with stripping E. I. kips. The kips are drummed with water and then with a stripping agent[1] and again washed with water; they

[1] A mixture of washing soda and ammonium sulphate is very suitable and the intensity of the stripping action can be regulated by the proportion of the two substances; equal quantities (say 3 per cent. on the weight of the wet leather) are convenient for use as a start, and excess of soda will intensify the action, while excess of ammonium sulphate will moderate it.

Digitized by Google

are then drummed a few hours with a 3 to 5 per cent. solution of Neradol D, which can be repeatedly used and strengthened for every new pack. The goods may then be dyed and fat liquored[2] and finished for box, or they may be buffed, dyed and drum-stuffed, etc., for mat finish.

Combinations of Neradol D with chrome tannage, alum tannage and formaldehyde tannage have also been tried successfully, and the bleaching effect on chrome tanned goods deserves to be specially mentioned. It is indeed possible to produce a chrome leather of nearly white color by simply suspending the well chromed goods in a 5 per cent. Neradol D solution until the desired color is reached.

These few examples may be sufficient to show that new and valuable effects can be obtained by the action of this artificial tannin and that the results justify the conclusion that the problem of synthetic organic tannins of technical importance is now solved.

A CONTRIBUTION TO THE HISTORY OF A NEW INDUSTRY.

By Dr. A. Muller-Jacobs.

About fifteen years ago, an article, which was destined to attract wide interest in industrial circles, appeared in almost all of the chemical papers, concerning a semi-official observation of Dr. Liebreich of Berlin—the great scientist, and inventor of "Lanolin." It was asserted that by the addition of a relatively small quantity of a certain substance with a high melting point to other substances of lower melting points,—as, for example, to waxes, stearin, paraffin, etc., the melting point and the hardness of such substances could be enormously increased. The substance used by Dr. Liebreich for his experiments was "Stearanilid." This innovation, if found to be true, would have been of great value, especially for the candle industry, where the melting point of the materials used plays the most important part.

After careful examination and repetition of Dr. Liebreich's

[2] Tanning dyeing and fat liquoring can be carried out simultaneously if desired, although the saving of time and labor will be balanced by the uneconomic way of using the tan liquor.

Digitized by Google

experiments, it was unfortunately found that his observations could not stand any scientific test, and proved to be a complete self-deception; but, curiously enough, this error in observation was as a fact to become the cornerstone of a now fast rising industry—the manufacture of Stearamid and its many new technical combination products—of which the Duron emulsions are an example.

The author of this paper—Dr. A. Muller Jacobs (of Turkey red oil fame, and also the first to propose and to introduce into the art of tanning, the Turkey red oils, which are sulphonated castor oils), was at that time chemist in the laboratories of the Arabol Mfg. Co., New York, and busied himself for a while with the above mentioned invention of Dr. Liebreich. In the course of his investigations, Muller-Jacobs also tried and studied the effect of the addition of small quantities of "Stearanilid" upon other substances than paraffin, stearic acid, waxes, etc.—such as all kinds of animal, vegetable and mineral oils (triglycerides), and found that the said substances, when mixed with a relatively minute quantity of "stearanilid," became emulsifiable—and emulsified easily and durably with distilled water. "Stearanilid" (its chemical formula being better stearic acid anilid, $C_6H_5.NH.C_{18}H_{34}COOH$) is easily formed by heating molecular quantities of stearic acid and anilin oil together in an appropriate apparatus for several hours. Water is formed, and stearanilid in theoretical quantities, which is afterward rectified by recrystallization out of alcohol, chloroform, or benzol. In its pure state, it forms fine needles with a melting point of 93.6° C. which have the above mentioned quality of easily dissolving by heating in waxes, mineral, vegetable or animal oils, etc.—rendering them emulsifiable in pure water. Later on, Muller-Jacobs found that the same properties, only in a far higher degree, have to be attributed also to certain amids of the fatty acid series; for example, to stearic acid amid or stearamid—its formula being $C_{18}H_{35}ONH_2$ and its melting point being 108°-109°C. This substance is easily formed by the heating of stearate of ammonia in a pressure kettle several hours at 150° C; the pressure inside the iron kettle being about 25 atmospheres equals 375 pounds per square inch.

Digitized by Google

The fact was soon established that stearamid had a far greater emulsifying power, weight for weight, than stearanilid; besides, the fact that the globules of the emulsified fats or oils are of a microscopic minuteness—a sure sign that they will keep unchanged a much longer time than those produced by stearanilid under the same circumstances.

As for the use of stearamid in the industries and arts, it was at first thought that certain of the fat or wax emulsions might furnish a good and cheap substitute for rosin soap in paper sizing; but it has not been found possible, as yet. But there is still a justifiable hope that it may yet be done. This would be of great value for the paper industry in general, as by the use of stearamid sizing, the paper would be increased considerably in quality, especially in durability,—stearamid not being affected by air or sunlight; both of which universal agents are known to shorten the life of paper sized with rosin soap. At the same time, it was also thought that such emulsions of oils or fats would doubtless be serviceable in the spinning of wool in place of the so-called various "Schmalzole." This has proved to be true—and the stearamid emulsions are already in the market for that purpose, and their use is progressing rapidly. Everybody knows that enormous quantities of fats and oils, and preparations of these materials of different makes, are used in the tanning industry, and already stearamid emulsions are being used in rapidly increasing amounts in practically every branch of the tanning industry.

A NEW EMULSIFYING AGENT, AND ITS APPLICATION TO TANNERY PRACTICE.*

By E. D. Van Tassel, Jr.

The amids of the higher fatty acids, of which stearamid is a typical example, have the peculiarity, as do the physiological amids, like lecithin, tyrosin, etc., of remaining suspended in minute division in watery solution with the power of lastingly emulsifying considerable proportions of neutral fats and oils.

Stearamid is a snow white crystalline body, glossy like mother of pearl. It melts at 230° F., and then has the appearance of a

* This and the preceding paper were read before the New England Section, S. C. I., at Boston.

Digitized by Google

waxlike body. Its formula is $C_{17}H_{35}CONH_2$. It resists acids and alkalies to a large extent, and like waxes and paraffins, it is indifferent to and resists most other chemicals, and has the advantage of being a uniform chemically defined compound.

Owing to the high melting point of stearamid, and to facilitate its use by the tanner, it is furnished in the form of a paste, called by the trade name "Duron," which is made by melting stearamid, adding some water and a small quantity of a protective colloid.

Stearamid keeps in emulsion from five to fifteen times its own weight of such oils as neatsfoot, moellon degras, fish oil, and other oils commonly used in the leather trade. But in addition to producing fine emulsions of these substances, it also produces emulsions of substances which formerly could not be practically emulsified, such as tallow, some mineral oils and paraffin wax.

In producing emulsions with stearamid or duron, the duron is placed in a steam-jacketed kettle at a temperature of from 185 to 200° F. Then the oil or previously melted grease or wax is slowly run in. Meanwhile a vigorous stirring action is continuously maintained. Then a suitable amount of water is added, stirring until an even pasty mixture is obtained. Such mixtures will keep indefinitely without separation, and may be easily thinned down as desired for use.

Stearamid emulsions practically destroy the odor of animal oils and greases, and greatly diminish that of fish oils. Stearamid has also a decided preservative action. The extremely minute globules from 0.001 millimeter to 0.005 millimeter in diameter—much more minute than those obtained by the usual methods of emulsification—insure thorough, rapid and uniform penetration and uniform distribution through the leather. Stearamid forms a skeleton or framework which envelops the infinitely minute fat particles, and prevents them from conglomerating again. The emulsification being thus due to mechanical or physical action, rather than to chemical change in the material, allows the oils to retain all their original softening, nourishing characteristics and value.

The use of mineral oils of very heavy body—so that the loss by evaporation is eliminated—is made possible by the introduction of stearamid emulsions. These emulsions of heavy mineral

Digitized by Google

oil lubricate the fiber perfectly, and when used in conjunction with an animal or fish oil for nourishing the fiber, form very satisfactory fat liquors. The addition of paraffin wax, emulsified by stearamid to a fineness of globule of 0.001 millimeter, gives a "full feel," and improved "break," due to a filling action; and the effect is far superior to that produced by using the melted wax straight.

Stearamid emulsions, as furnished to the tanners, comprize the following raw materials: neatsfoot oil, lard oil, peanut oil, menhaden oil, cod oil, moellon degras, sperm oil, five grades of mineral oils from lightest to heaviest, soya oil, castor oil, corn oil, cocoanut oil, distilled wool oil, wool fat, tallow, stearine, paraffine waxes of 120° and 130°, montan wax, vegetable wax, and carnauba wax.

The application of the emulsions produced by stearamid to the leather does not differ from that of the older emulsions, produced largely by the use of soap and soda. The fat liquoring is done in the same manner, and generally under the same conditions. The tanner now has at his command an increased supply of fat liquoring materials in a uniform condition, and in a highly efficient form.

THE FILTER METHOD OF TANNIN ANALYSIS.

By Lloyd Balderston.

In April, 1912, the JOURNAL published a translation of an article by Dr. E. Schell in which he compared the shake and filter methods of analysis, and demonstrated to his own apparent satisfaction that the filter method is more nearly correct and should therefore be again adopted. In the current number appears an abstract of an article on "a new method of tannin analysis" in which the filter method is evidently regarded as the standard.

We have been waiting since April, 1912, for some member of our Association to come forward with an explanation of the reasons why the filter method has been abandoned in this country and in England. Evidently those who know, consider the matter one which has already been so thoroughly settled that no further

Digitized by Google

discussion is necessary. It has now been so long since the method was used in this country that only a minority of American leather chemists are acquainted with the process in a practical way, and the literature of the subject is in such back numbers of our periodicals[1] as to be inaccessible to many. I therefore presume to make one more statement of the case, in the hope of explaining to such as have not investigated the matter why the filter method is unreliable.

The method of determining non-tannins by the filter method is briefly as follows:—About 7 grams of dry hide-powder are packed in a glass bell having an opening at the small end into which the short end of a siphon is fitted by means of a rubber stopper. The bell is placed in a vessel containing the liquor to be detannized, and the siphon started. The first 30 cubic centimeters of solution coming over are rejected and the next 60 collected, from which 50 cubic centimeters are pipetted for evaporation.

If successive portions of 50 cubic centimeters each be collected, the solids contained increase successively, until tannin begins to come through, and the last portion free from tannin gives a non-tannin value approximately the same as that obtained by the shake method. This fact alone is sufficient to condemn the method. The fact that it gives lower non-tannins and therefore higher tannins than the shake method seems to be the reason why the extract makers of the Continent are unable to give it up.

If the analysis of tanning materials has any purpose at all, it is to draw as nearly accurate a line as possible between the tannins and non-tannins contained in the material under examination. If this be granted, what excuse remains for defending a method which adds to the tannin an arbitrary or indefinite amount of non-tannin? In a recent discussion at a meeting of the British Section of the I. A. L. T. C., Dr. Stiasny stated the general case very clearly. He said that in comparing two samples of hide-powder both of which give tannin-free filtrates, it is evident that the one which gives higher non-tans must be more nearly correct. This is manifestly and undeniably true, and the statement applies with equal force to a comparison between methods of analysis by means of hide-powder or other tannin-absorbing

* See the paper by H. C. Reed in this JOURNAL, Vol. I, pp. 288-307.

Digitized by Google

materials. The same point is well emphasized by Mr. H. G. Bennett in his paper on "Further Progress in Tannin Analysis," abstracted in this number.

H. C. Reed's paper in Volume I of this JOURNAL goes into the whole matter so thoroughly as really to leave nothing to be said. His conclusions are not drawn from theory, but from a great mass of experimental facts, and the investigations which he describes, demonstrate beyond question the superiority of the shake method for the determination of tannin.

ABSTRACTS.

A New Simple Method of Determining Sulphurous Acid in the Presence of Thiosulphates. A. SANDER. *Zietschrift angew. Chemie*, Vol. 27, p. 194. In using Feld's method for sulphurous acid, the author hit upon a simplification. Instead of titrating the free acid with NaOH, he begins by adding an excess of iodine, titrating the excess with thiosulphate. He then adds an excess of "iodide-iodate solution," from which the sulphurous acid liberates iodine. This liberated iodine is titrated with thiosulphate. L. B.

New Method for Rapid Determination of Tannin in Chestnut Extracts. LEON EGLENE, Professor in the School of Commerce and Industry at Mazamet. *LaHalle aux Cuirs*, Technical Part, March 22, 1914. The method is not new, being identical with that proposed by Vanicek in *Zeitschr. f. angew. Chemie*, an abstract of whose paper appeared in this JOURNAL for March, 1913, page 150. The method consists in titrating the liquor, suitably diluted, with N/10 soda, phenolphthalein indicator, and then detannizing an equal amount of solution with gelatine, filtering, washing the precipitate and titrating the whole filtrate. The difference in the two results is calculated to tannin by multiplying by a factor which must be determined beforehand for the particular kind of extract by comparison of the result of titration with that of a gravimetric analysis. The analyses which the author uses for comparison in his examples are made by the filter method. The factor used is obtained by treating 50 cc. of solution containing 0.3 gram tannin by the two methods. The result shows 1 g. tannin equivalent to 3 cc. of N/10 soda. Five other comparative analyses in which this factor is used show differences ranging from 0.05 to 0.53 per cent. L. B.

[Translator's Note.—The volume of N/10 soda used in the titration is only 0.9 cc. Since this amount could hardly be certain within 0.05 cc., it is evident that variations of 0.5 per cent. in 30 per cent. are not unexpected. Careful use of a Baumé hydrometer would enable one to com-

Digitized by Google

pare different samples of the same extract quite as accurately as this, and the author only recommends his method for extracts which are strictly comparable with each other.]

Guara. W. EITNER. *Gerber*, April 1, 1914. A so-called new tanning material under the above name, and an extract made from it, were submitted to Mr. Eitner for examination. Guara is the name given in Brazil and Colombia to a tree or shrub whose Latin name is Paullinia sorbilis. The material came in powdered form, being evidently a ground pod, seeming like a sort of divi, and it agreed in character and analysis with a material described in *Gerber* for Feb. 1, 1890, under the name of cascalotte, a kind of divi. Again in Jan., 1903, a notice appeared in *Gerber* of a new tanning material from Oaxaca, Mexico, a kind of divi called cascalotte. The tannin content of the "guara-meal" is about 55 per cent. It makes a very light colored brownish yellow leather. The extract had less tannin than the unleached material, about 42 per cent. The tannin is of the catechol class, like divi. L. B.

Imported Raw Vegetable Tanning Materials. JOHN H. YOCUM. *S. & L. Rep.*, Mar. 19 and April 9. Excepting sumac, raw tanning materials were not imported into the United States in important quantities previous to 1902. The value of such imports in 1912 was $1,770,000 and in 1913, $1,635,000. The most important materials are myrobalans, valonia, mangrove and sumac. As quebracho wood is not handled by tanners in the raw condition, it is not included in the discussion. The chief shipping point for valonia is Smyrna. The dealers of that city sort the valonia, and in recent years make a large number of grades. The cups average about 30 per cent. tannin and the beard about 41 per cent. Importations for 1913 amounted to about $250,000. The bulk of myrobalans imported are "J's"; the total value for 1913 being about $250,000. No. 1 averages about 35 per cent. tannin and No. 2 about 30 per cent. Sicilian sumac averages about 30 per cent. tannin; Virginia about 21 per cent. Importations in 1912 amounted to $280,000 and in 1913 to $218,000. Divi-divi is closely related to tari, algarobilla and cascalote. It contains about 45 per cent. tannin, and 10 per cent. sugar. Tari pods come from Burma, containing nearly as much tannin as divi-divi. Mangrove bark was imported from Africa in 1912 to the extent of 17,500 tons, and in 1913, 11,000 tons. It is at present prices the cheapest tanning material.

Preventing Salt Stains and Loss of Weight by Decomposition. *S. & L. Rep.*, April 16, 1914. U. S. Patent 1,091,236, issued to C. C. Moore and W. Trantom of England, covers the treatment of hides immediately after removal from the carcass with chemically pure common salt in powdered form. The patentees claim that a saving of from 2 to 4 per cent. of hide substance is made which would otherwise be lost by the formation of soluble hide compounds. From 10 to 12 pounds of salt per hide are necessary.

Digitized by Google

The Prevention of Salt Stains. JOHN H. YOCUM. *S. & L. Rep.*, April 2, 1914. The prevention of salt stains demands a material which will (1) prevent oxidation of the iron of the blood, (2) be alkaline, thus aiding the free drainage of the blood from the hides, (3) be germicidal, (4) not interfere with the cure of the hide and (5) not be too expensive for commercial use. Mr. Yocum has devised a preparation to be mixed with common salt, which he recommends as fulfilling these five requirements. It is sold under the name 'Cyko."

Tannin Bearers of South America. H. G. CUTLER. *Hide and Leather* April 4, 1914. By the consolidation of the Forestal Company with the Santa Fe Land Company, 6,000,000 acres of land are brought under one management. The capitalization of the new corporation is $10,000,000. Information is given in regard to extract manufacture, some of which is truly astonishing. The consumption of water in an extract factory is several thousand cubic meters daily. In some districts fresh water cannot be had, and it is necessary to distil all the water used. The wood is prepared for extraction by splitting the logs into boards. Any one who has ever worked a piece of quebracho wood will be greatly interested to learn of this method of dividing the logs. After the wood is extracted, it is used for fence posts, beams, paving blocks, railroad ties, firewood and other purposes. The use of spent wood as fuel is familiar, but the other uses mentioned are a real surprise to some of us untravelled leather chemists.

Shoe Trade of Argentina. *Chamber of Commerce Journal*, London, through *Hide and Leather*. At the time of the census of 1910 there were 227 tanneries in Argentina, employing 3,389 persons, and 254 shoe factories, employing 8,000 workers. The shoe industry is protected by heavy duties. In 1912 there were imported 45,262 dozen pairs of boots and shoes, valued at $629,746, coming chiefly from England and the United States. Eleven glove factories produce about $166,000 worth of gloves yearly.

Economical Leather Manufacture. M. C. LAMB. *S. & L. Rep.*, March 19, 1914, p. 31. Several instances are given in which materials have been wasted because of lack of chemical knowledge on the part of the tanner. When 5 per cent. potassium bichromate and 2½ per cent. hydrochloric acid are used in the two-bath chrome process (Schultz's formula), one-third of the bichromate is wasted.

Use of Spruce Extract in Tanning. CHAS. M. PROCTOR. *S. & L. Rep.*, March 19, 1914, p. 39. In a sole leather yard, after 35 to 45 days in vegetable liquors, the stock may be taken from the vats, wrung, and drummed with full strength spruce extract, 10 pounds per side, put in at 105° to 115° F. After drumming 1½ to 2 hours, the leather is taken from the drum and placed in a spruce tempering liquor of 60° to 80° bk.,

Digitized by Google

where it lies from 7 to 10 days, at 90° F. This liquor may be used repeatedly, and the quality of the product depends on a proper use of the tempering vat. Spruce extract may also be used as a hot dip, and for retanning any kind of chrome leather.

A Study in Yellow. CHAS. A. MCNEIL. *S. & L. Rep.*, March 19, 1914. p. 41. A discussion of the properties of yellow leather, and the use of yellow dyes.

Further Progress in Tannin Analysis. H. G. BENNETT. *S. & L. Rep.*, March 19, 1914, p. 45. Methods of tannin analysis, both of the American and European associations, report more tannin in materials examined than they really contain. The error is different with different materials. Of two materials, each reported as containing 30 per cent. tannin, one may have 28 per cent. and the other 26 per cent. Different tannins have different leather-forming value, but this has nothing to do with the problem, being the tanner's affair entirely. The chemist's business is to tell how much tannin is present, not to pass an opinion on its leather-forming value. Another question which is also not involved is the leather-forming value of non-tans. Even if these have such value, that is no reason for calling them tannin, and the smaller the amount of non-tans included in the "tannin" reported, the truer the result. The leather-forming value of non-tans is still a matter of dispute, and certainly does not warrant including an indefinite portion of them as "tannin." The greater the amount of non-tans in a material, the greater the error due to inclusion of non-tans is likely to be. (Analysis of a spent liquor showing no reaction for tannin with gelatine-salt will generally show "tannin" in appreciable quantity.—ED.) A method of analysis is to be desired which will distinguish better between real tannins and those astringent non-tans of which gallic acid is a type. Any improvement in the method must show more non-tans and less tannin. Mr. Bennett appeals to American leather men to consider the possibility of agreeing on an improved method. He has found that certain modifications in the I. A. L. T. C. method give 3 to 4 per cent. more non-tans than the official method. (Mr. Bennett does not make clear on what base this 3 or 4 per cent. is reckoned. We assume that the refers to extracts such as are alluded to before, containing up to 30 per cent. tannin.) The modifications are as follows: (1) decreased acidity in the hide-powder before chroming for analysis; (2) detannization in more dilute infusion; (3) use of less hide-powder; (4) decreased acidity in the hide-powder due to chroming, which may be accomplished by using a more basic salt.

Estimation of Free Sulphuric Acid in Leather. J. PAESSLER. *Collegium*, March, 1914. The methods of estimation heretofore used fail when the leather contains sulphur compounds which are liable to yield free sulphuric acid in consequence of the processes to which the leather is sub-

Digitized by Google

jected in the course of analysis. The fundamental error inherent in the methods is the fact that they estimate the sulphate-ions and not the constituent which is characteristic of free sulphuric acid, the hydrogen ions. They also have without exception the drawbacks which always attach to an indirect method. It is therefore imperative to seek a method which avoids these errors and difficulties. The Freiberg Research Institute has found a process for the "dialysis of leather" which affords a trustworthy means of determining whether a sample of leather contains free sulphuric acid or not. The quantitative side of the process is not yet fully worked out, so the present paper is to be considered as a report of progress, following Dr. Paessler's announcement (published in the February JOURNAL, p. 87).

If completely neutral hide be treated with dilute sulphuric acid, the quantity of hide and of solution being unchanged, but the quantity of acid being varied, so as to give acid solutions of varying strength, a long series of experiments has shown that the more free acid is offered to the hide, the smaller the percentage of this acid taken up by the hide, and the smaller the amount of free acid offered, the larger is the percentage of it which is taken up. In no case, even with the use of the smallest quantities of acid, was all of the acid taken up, but a plainly observable residue always staid in the solution. These results make it apparent that the taking up of sulphuric acid by hide is a pure adsorption process. If this conclusion is correct, the process must be reversible; that is, if the hide is placed in pure water it must little by little give back to the water as much of the adsorbed sulphuric acid as is necessary to establish a new equilibrium between the solution outside of the hide, and the sulphuric acid which the hide retains. Research along this line brought full confirmation of this hypothesis. The more free sulphuric acid the hide contains, the more it gives up to the water, and the less it contains, the less it gives up. From the reversibility of the process it must be concluded that hide which contains free acid must always when placed in pure water give up to the water a part of its acid. Since very slight traces of free sulphuric acid in water may be detected, the qualitative test for acid in hide by this means is seen to be reliable. If the test shows no acid in the water, it is certain that the hide contains no free acid. Since the taking up and giving out of acid by the hide take place in accordance with definite laws, there is a good prospect that a quantitative method may be developed. Experiments looking toward such a method are in progress.

To leather in the early stages of tannage, the test may be applied in the same manner as to hide. When leather already tanned has opportunity to absorb free sulphuric acid, as for instance in the bleach, it behaves in the same manner as hide, and a part of the contained acid will always be given up if the leather is soaked in pure water. Other water-soluble materials in the leather will in general interfere with the test. This difficulty has been met by putting the leather to be tested into a vessel of pure water, having parchment walls, and placing this in a vessel

Digitized by Google

of pure water. The sulphuric acid by reason of its high diffusion constant diffuses through the parchment much more rapidly than the substances of high molecular weight which also soak out of the leather. The water in the outer vessel may now be tested with methyl-orange, potassium-iodide-potassium-iodate solution or otherwise.

The further working out of this method is in the hands of Mr. Glaab.

L. B.

Distinguishing and Testing Tanning Extracts. R. LAUFFMANN. *Leder-techn. Rundschau*, 1914 [6], 33-7, 41-4, 49-54, 60-1. Tannin may cost from 0.36 to 1.80 marks per kilo according to source and also vary in tanning effect. Its differentiation is therefore of practical importance in the valuation of extracts and detection of adulterants. The author's extensive review of the entire subject is based on the Stenhouse-Procter division of the tannins into the two primary groups: *catechol tannins* including quebracho, mangrove, mimosas, mallet, fir, hemlock, elm, gambier, catechu; *pyrogallol tannins,* including chestnut, oakwood, myrobalans, divi-divi, valonia, algarobilla, sumac, knoppern. Oak bark contains chiefly catechol tannin with small amounts of pyrogallol tannin. The distinctive tests used in this analysis are affected by the presence of clarifying agents. Certain general determinations are useful. For uniform water content (60 per cent.) the specific gravity of catechol tan extracts (untreated) is lowest, 20-21° B. for quebracho up to 24 for mimosa, while that of the pyrogallols is about 25. Pure quebracho or chestnut have low ash (0.5 per cent.) and higher numbers indicate presence of minerals or high ash tanstuffs. Absence of NaCl denotes absence of mangrove; the salt when present may be due to other sources. The group reagents are fully discussed. (1) Stiasny's formaldehyde reaction (this JOURNAL, 1911 [6], 486; 1912 [7], 550) precipitates catechol tans completely, pyrogallols not at all, or slightly; these are detected in the filtrate by Fe. color test. Cellulose extract does not give this, but may be detected by the Procter-Hirst reaction. (2) Stiasny's lead acetate reaction (loc. cit. above) reverses the above, precipitating the pyrogallols completely, the others not at all, or partially. Lead sulphate or sulphite are also precipitated from sulphited extracts. (3) Garancine dyeing test (Paessler); about 25 cc. of the tannin solution (analysis strength) are diluted to one liter, this solution boiled ½ hour each with 7 to 9 successive strips of garancine (madder dyed goods). Lakes of characteristic colors are thus produced enabling in general the two groups to be distinguished, singly or in mixture, by color and order of formation. (4) Bromine water (Procter) precipitates the catechols but not the pyrogallols. Cellulose extract according to Stiasny hinders the normal precipitation; strongly sulphited extracts also lessen the reaction.

The two principal groups may be sub-divided by the following reagents. (5) Lauffmann's molybdenum test (JOURNAL, 1913 [8], 55) gives the following Mo numbers:

Digitized by Google

Catechol tans:	
Quebracho	3-37
Pine bark	26-43
Hemlock bark	64-82
Elm	42
Gambier	0-13
Catechu	0
Mangrove bark	100-135
Mimosa bark	110-129
Oak bark	135
Pyrogallol tans:	
Myrobalans	80-140
Sumac	128-154
Divi-divi	150
Chestnut wood	182-225
Oak wood	176-206
Valonia	185-222

These numbers diverge sufficiently to permit many mixtures being detected, provided cellulose extract is absent; this lowers the number. (6) The ammonium sulphide reaction (Eitner-Philip; JOURNAL, 1909 [4], 249) is especially useful when only catechol tans are present. Of these quebracho, mangrove, pine, catechu and gambier are not precipitated, while mimosa, mallet, oak bark and hemlock are precipitated.

The tests of the individual tanstuffs and their constants follow in full detail and cannot well be condensed here. Most of the distinctions appear in Stiasny's reports printed in the JOURNAL. W. J. K.

Sulphite-Cellulose Lye as Tanning Agent and Its Determination in Leather. W. MOELLER. *Ledertechn. Rundschau,* 1914 [6], 81-6. The attempt to utilize wood extract for tanning is an old process historically, and after its failure the cellulose industry itself developed. Cellulose lye, now the by-product, is again being essayed in leather making and opinions vary as to its value. It is claimed especially, to impart great weight, to improve the qualities of other materials in mixture, to dissolve difficult soluble tans and to brighten dark extracts or tanned leather.

Filling and loading are terms often used as equivalent but properly express two different ideas. Filling leather with excess of extract in the drum or vats is a normal completion of tannage and gives the leather useful properties. Materials which are forced into the leather by heating or impregnation and drying are simply loading or weight giving substances, generally lowering the quality. Used in this way tans and non-tans are impregnated alike and when considering sulphite-cellulose in this light, it is immaterial whether tans be present at all.

The contradictions in the statements concerning detection of sulphite-cellulose in leather are explained by failure to take account of the manner in which the material has been applied. In agreement with Loveland, the

Digitized by Google

author finds that extracts of leather tanned with sulphite-cellulose do not give the Procter-Hirst reaction. This is explained by the extreme difficulty of dissolving out the substance giving the reaction (lignin sulpho-acid) which is itself a minor ingredient of the extract; when used in the tanning process proper, this becomes firmly attached to the fiber and is not removed by hot water. On the other hand, when used for mere impregnation, the cellulose is easily extracted and detected in analysis.

The following experiments were made bearing upon this question, neradol also being included, since it likewise gives the Procter-Hirst reaction. Samples of white pelt were respectively tanned with: (1) pure cellulose extract; (3) neradol; (4) ½ cellulose, ½ quebracho; (5) ½ quebracho, ½ neradol; (6) ½ cellulose, ½ quebracho, after-tannage with pure cellulose; (7) ½ quebracho, ½ neradol, after-tannage pure neradol. All of these were washed and their extracts gave no Procter-Hirst reaction. No. (2) was fore-tanned with pure quebracho, then impregnated (loaded) with sulphite-cellulose in the usual way. That is, the moist through-tanned leather was brushed with cellulose extract and let dry. The H_2O extract from this leather gave a strong reaction. That sulphite-cellulose (or neradol) was really absorbed in all these leathers the author proved by extraction with 2 per cent. NaOH at ordinary temperature for 12 to 24 hours or even longer, according as the leather was slow in swelling. The extract was slightly acidulated with HCl, filtered and tested according to Procter-Hirst. A new series of leathers thus treated gave: (1) pure cellulose tannage, strong reaction; (2) pure neradol, strong reaction; (3) tanned through with quebracho, after-tannage cellulose, no reaction, confirming practice that an after-tannage with cellulose does not increase the rendement; (4) similar experiment with neradol, strong reaction showing that it is taken up. It is doubtful if this is of real advantage since large amounts of vegetable tans are dissolved out by neradol during such an after-tannage. (5) Tannage with ¾ quebracho, ¼ cellulose, no reaction; (6) ¾ quebracho, ¼ neradol, slight reaction; (7) (8) ½ quebracho, ½ cellulose (or neradol), strong reaction. Extraction with warm alkali gave no tests.

The author regards his method as an important addition to leather analysis, enabling one to detect foreign admixtures in vegetable tanned leathers. It further confirms a view already expressed by others, that hide preferably absorbs vegetable tans while these last leaving the cellulose lye to accumulate in the liquors and weaken their effect. On that account the use of cellulose extract to dissolve insoluble quebracho should be rejected. The only value it may have is for loading and although it does not exude like glucose it makes the leather brittle which must be prevented in after treatment. In conclusion, this material has no tanning effect whatever and while apparently cheap is one of the most expensive loading agents used. W. J. K.

Digitized by Google

THE COLLOID'S LAMENT.*

By Ellwood Hendrick.

I am a simple colloid,
The place that I live in
Is very much restricted for
I cannot get through skin.

I've neither shape nor figure,
I am not crystalline,
And this it is that breaks my heart—
My gosh, how I repine!

I want to be geometric,
Have sides and angles true,
And yet I'm bound as hydrosol
Or gel to be like glue.

Electrolytes disturb me,
They almost drive me mad,
And usually they knock me down
Which pains and makes me sad.

Dialysis deludes me
As I have said before,
I'm all shut in while crystalloids
Find many an open door.

I'm sticky and I'm gummy,
I am the soul of dirt,—
To be like that and know it too,
Just think how it must hurt!

I'm scorned and I am hated
And gen'rally despised,
Professor Ostwald stay with me
And make me civilized!

I want a def'nite figure
Of any standard shape
So that I can from this blamed mess
Eventually escape.

* Read at the dinner to Wolfgang Ostwald, N. Y. Chemists Club and printed in *The Percolator*, April 18.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. IX JUNE, 1914 No. 6

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1914, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VEITCH, } . . . Past Presidents

OFFICERS, 1913-'14

PRESIDENT—W. K. ALSOP, Ridgway, Pa.

VICE-PRESIDENT—C. W. NORRIS, 80 South Street, New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

LLOYD BALDERSTON, Ridgway, Pa.

C. R. OBERFELL, Harrisonburg, Va.

T. A. FAUST, 323 Academy Street, Newark, N. J.

CHANGES OF ADDRESS.

Chas. A. Reisig, to Wissahickon Apt. C-5, Germantown, Philadelphia, Pa.

Dr. P. H. Voiges, to 1046 E. 14th St., Flatbush, Brooklyn, N. Y

PROPOSED CHANGE OF METHODS.

The following change has been proposed in writing to the Secretary in accordance with paragraph 22 of the By-Laws, A. L. C. A.

To be added to note following (7) (B), under Analysis of Extracts:

In all cases where the effect of rapid cooling is not known to be negligible, the analysis shall be performed under option (b).

Digitized by Google

FURTHER NOTES ON ENZYMES.[1]

By Joseph T. Wood.

It seems to me that the most mysterious and wonderful of all the unexplored regions of science is the problem of the constitution and mode of action of enzymes. When we find that the most minute quantity, less than one tenth of a mg. of a preparation, which we know is still very far from being the pure enzyme, is capable of setting in motion, and effecting chemical changes, which result in the transformation of matter 200,000 times its own weight; when we further consider that if we wish to bring about similar changes in the laboratory, we must employ powerful acids or alkalis, and high temperatures, and beyond this, when we find that there exist hundreds, perhaps thousands of enzymes, each of which appears to be constructed and fitted only to bring about just one particular decomposition or synthesis, and that, notwithstanding the immense progress of chemistry, we know nothing whatever of the constitution of these marvelous bodies, but have hitherto been able merely to record the facts and the conditions of our observations, when we consider all these things we may be able to put ourselves in the place of those ancient alchemists in whom religion and science were closely united. These men, in addition to the search for the philosopher's stone, sought for the elexir vitae, they believed in the vital principle to which, after trying to explain everything in terms of mechanics, we seem to be coming back. Paracelsus says of them "These do not give themselves up to ease and idleness, but they devote themselves diligently to their labors, sweating whole nights over fiery furnaces. These do not kill the time with empty talk, but find their delight in their laboratory."

I suppose I ought to be sweating in the laboratory instead of talking. I propose, nevertheless to give a very brief account of some recent discoveries about enzymes. These are scattered through a number of papers and perhaps are not available to everyone.

[1] Paper, read at the Meeting of the British Section of the I. A. L. T. C. in connection with the Nottingham Section of the Soc. of Chem. Ind. in Nottingham, November 1913. From *Collegium*, 1914, pp. 123-6.

Digitized by Google

One of the first observations made on enzymes was that they are destroyed by heating to 100° C. very much in the same way as living organisms are killed by heat, at any rate in the presence of water.

A Russian biologist (Kulpsohn) was I believe the first to observe that the oxydase enzyme of the radish which had lost its properties by boiling, regained them on standing exposed to the air. Another Russian-(Gramenitzki) has followed up the subject in order to discover whether such regeneration occurs with other enzymes. He examined the action of a Japanese diastase "Taka" and of maltin on rice starch, following the hydrolysis by 3 methods, by means of the polariscope, the iodine reaction, and titration of the sugar produced with Fehlings solution. Special precautions were taken to keep both the ferment and the starch solution sterile. He found that the taka diastase even after heating to 115° for ¼ hour recovered its properties to a greater or less extent.

The time required for regeneration and the degree of regeneration depend on the temperature and time of heating and the temperature at which regeneration is conducted. The longer and stronger the heating, the slower and less complete is the regeneration, until finally the enzyme is permanently destroyed. No regeneration takes place at 50° C., but it is most rapid at 40° C.; at the ordinary temperature regeneration is much slower, but it is more complete than at 40° C. The author quotes experiments to prove that the regeneration is not due to the survival of traces of active enzyme after the heating. The oxydase of the preparation known as "maltin" is also rendered inactive by heating at temperatures above 80° C., and is likewise capable of regeneration on cooling after having been heated for 15-30 minutes at 100° C.; the solutions of this oxydase in their temporarily inactive state possess a positive deoxidizing action towards guaïacum blue. The amylase (starch liquefying enzyme) of "maltin" is capable of regeneration after 10 minutes at 100° C. but not after 15 minutes; the amylomaltase (saccharifying enzyme) on the other hand appears to be permanently destroyed by heating up to 100° C.

Similarly, the various component enzymes of "taka diastase"

Digitized by Google

behave differently after heating. When the solution of "taka-diastase" is heated to 70° C., the catalytic enzyme is destroyed but the inverting and diastatic functions remain active. On further heating to 100° C. both these activities are paralyzed, but the diastatic function is capable of regeneration, whereas the inverting function is permanently destroyed.

A very pretty method of estimating quantitatively the relative amount of a tryptic enzyme is that of Grützner, which has been used by O. Palladin[1] to determine the law of fermentation by trypsin. Fibrin is dyed by means of spirit blue (Bayer); this color is quite insoluble in water, as is also the fibrin, but when the latter is acted upon by trypsin it is rendered soluble, and the liquid is colored blue. An extremely small amount of ferment may thus be detected, and from the intensity of the color conclusions may be drawn as to the velocity of the digestion, and therefore of the relative ferment content of the solution.

The various ferments existing in animal and vegetable bodies are generally quite specific in their action. This specificity in the case of the sugar splitting ferments is well known, but in the case of secretions like the pancreatic and intestinal juices and extracts of various animal organs obtained by pressure, it has hitherto been extremely difficult to differentiate the various component ferments. Abderhalden was the first to propose the use of the polypeptides (synthesized by Emil Fischer) for this purpose. He uses optically active polypeptides, of strong dextro rotatory power, whose components under the conditions of the experiment have no rotatory power, *e. g.*, d-alanin: under the action of the ferment the rotation diminishes and thus the course of the hydrolysis can be followed quantitatively. Since the structure of these synthetic polypeptides is exactly known, definite conclusions may be drawn from the change of the rotation.

Koelker has employed a simpler body, racemic alanylglycin, for the same purpose. Here the original substance has no optical activity but under the action of the enzyme one component or the other is acted upon and so a rotation of the plane of polarization is caused.

Abderhalden and Koelker showed that l-leucyl-glycin which is

[1] Ueber eine einfache quantitative Trypsinbestimmung und das Fermentgesetz des Trypsins, (Koch 1910, 649) Pflügers Archiv Bd. 137, 337.

Digitized by Google

not attacked by the pancreatic juice, is hydrolyzed by a mixture of pancreatic and intestinal juice: but glycyl-d-alanin withstood the action of the combined ferments.

In the hydrolysis of l-leucyl-glycin-d-alanin by a mixture of pancreatic and intestinal juice, dextro-rotation first occurs; and as digestion proceeds the following figures were obtained:

$$+20°+10°\ 0°+2.4°+85°-50°$$

indicating that first d-alanin is separated, then the remainder l-leucyl-glycin is split up into its components.

In the digestion of glycyl-d-alanin-glycin:

$$-64°\ 0°+2.4°+50°-50°.$$

Although the indications demand a good knowledge of the constitution of the polypeptides, the above outline shows that the method can give important information as to the course of the digestion.

The method has been used to study the enzymes secreted by bacteria.

The occurrence of tryptic enzymes in plants is of course common knowledge, for instance papaïn (in the juice of Carica papaya). Blood has recently prepared erepsin (an enzyme of the intestinal juice) from cauliflowers. The juice obtained by pressure was rich in sugar and about N/50 acid to phenolphthalein. It was dialyzed for 41 hours through parchment against running water. The filtrate of the dialysate was saturated with Ammonium sulphate. On standing in the cold a flocculent precipitate was obtained. It was dissolved in water, the solution filtered and dialyzed for 6 days against running water. The resulting clear solution is pale yellow and neutral to litmus. Toluol was used as antiseptic. The solution hydrolyzed Witte's peptone in alkaline and neutral solution. Acidity of the solution to positive methyl-orange reaction acted adversely. After 1-3 days the tryptophan test with bromine water was positive. HCN activated the hydrolysis. On standing with Roche's peptone for 3 days at 40° tyrosin crystallized out. Casein digested for 17 hours gave the tryptophan reaction. The enzyme coagulates milk and liquefies gelatin. It further resembles the erepsin of intestinal juice in not acting on fibrin or coagulated egg albumen. The temperature optimum is from 40—50° C.

Digitized by Google

The above is an example of an intracellular enzyme, of which many are now known. Liver, muscle and kidney, all contain very energetic proteolytic enzymes which act in an analogous manner to those of the pancreatic juices. The blood serum also contains similar enzymes, and of course the leucocytes of the blood also. These enzymes have been obtained by submitting the various organs and tissues to a pressure of 300 atmospheres.

Abderhalden and his pupils have investigated the action of these tissue juices on synthetic polypeptides. Two to three cc. of the juice obtained as above are added to a watery solution of peptide, some toluol is added and the solution kept in the incubator at 37-40° for 3-4 days. It is then examined in the polariscope as above explained.

With the exception of leucyl-leucin the racemic peptides are split asymmetrically.

Glycyl-l-tyrosin was found to be a very good material for classifying proteolytic enzymes. Yeast juice, (which contains several enzymes) split glycyl-glycin and glycyl-l-tyrosin very energetically. The proteolytic enzyme was still active after the zymase was killed. The products of the hydrolysis are always the active amino-acids which form a constituent of the proteins. Ox blood and dog blood sera also hydrolyze glycyl-l-tyrosin.

The most fascinating problem of all is that of the synthetic production of enzymes.

Since we do not know what an enzyme is, we may assume that the problem at present is insoluble. A starting point for such a work has, however, been made by Wolff and Fernbach, who found that starch paste is rapidly oxidized by the combined action of peroxide of hydrogen, (H_2O_2) and sulphate of iron ($FeSO_4$). At 65° C. an almost instantaneous liquefaction of the starch is brought about.

A peroxydase was imitated by means of a mixture of 33 mg. K_4FeCy_6 + 3 aq. in 40 cc. water and 35.6 mg. $FeSO_4$ in 200 cc. water.

The above authors conclude from experiments with such colloidal ferrocyanate solutions that "The specificity of an oxydizing catalyst (here iron) is a function of the chemical combination of which it forms a part; *i. e.*, that the specificity alters with

Digitized by Google

the nature of the organic compound with which the metal is combined."

It would, therefore, seem to be possible by the introduction or substitution of new substances into such compounds to change their specific action, in other words to produce new enzymes. I have touched upon this subject in the German edition of my book on the bating of skins (p. 113), and hope to find time to come back to it in a future paper.

Nottingham, November 16th, 1913.

METHODS OF CHROMIUM DETERMINATION.

By L. Balderston.

The writer was appointed by the Council as chairman of a committee to frame optional methods of analysis for chrome liquors, other materials used in chrome leather manufacture, and other materials not at present mentioned in our official and provisional methods. The purpose of the present paper is to invite from the members of the Association suggestions and criticism in regard to methods of chrome determination.

The methods used in this laboratory are essentially those outlined in Procter's "Leather Industries Laboratory Book." For basic chrome liquors we aim to use dilutions whose content of Cr_2O_3 shall be from 0.15 to 0.2 per cent. Ten cc. of such a liquor are pipetted into an Erlenmeyer of 250 or 300 cc. and further diluted to about 50 cc. About 2 grams of sodium peroxide are then added to convert the chromium into sodium chromate, and after thorough mixing the whole is boiled gently for 30 minutes to insure the expulsion of all the free oxygen released by the Na_2O_2. After cooling, the solution is neutralized with HCl. No indicator is necessary, as the change of color from yellow to orange, due to the conversion of chromate into bichromate, is a sufficiently close test of neutrality. Five cc. excess HCl are then added, and the solution again cooled. It is most convenient to run in the acid from a burette.

To the cooled solution, 10 cc. of a 10 per cent. solution of potassium iodide are added, an amount of iodine corresponding

Digitized by Google

to the bichromate present being set free. The solution should stand about a minute before titrating the iodine with sodium thiosulphate, to allow time for the reaction to be complete. It should not stand as much as five minutes, however, as a slight reversal takes place, and too low a result may thus be obtained. When enough 0.1 N. thiosulphate has been added nearly to discharge the iodine color, a little starch solution is added and the titration completed. The end point is very sharp, the blue of the starch giving place to the pale green of the chromium chloride. Sometimes, from one cause or another, the solution is violet instead of green when the end-point is reached, the chromium chloride being in the "violet modification." The violet color generally changes to green in one or two minutes. Often the starch blue returns after a few minutes, due to the reversal above mentioned. Each cc. of thiosulphate used is equivalent to 0.002533 gram of Cr_2O_3. Ten cc. of a liquor having 0.2 per cent. Cr_2O_3 will thus require nearly 8 cc. of thiosulphate. When the liquors examined are very weak, it is well to take more than 10 cc., so that the amount of thiosulphate required shall not be less than 5 cc.

It is very generally necessary to determine the acid in one-bath chrome liquors, and for that purpose this laboratory uses the method of the "L. I. L. B." Fifty cc. of the same dilution used for the Cr_2O_3 determination are diluted to about 450 in a porcelain dish and heated to boiling. One cc. of a 5 per cent. solution of phenolphthalein is added and 0.5 N. caustic soda run in. The red first appearing vanishes on further boiling. The end-point is reached when a faint pink persists after boiling one minute. The color deepens as the solution cools. Of course this determination includes all acid combined with Cr and all (if any) that was free in the liquor. There is no practicable method of distinguishing between them, so far as I know. One cc. of 0.5 N. NaOH is equivalent, of course, to 0.0245 gram of H_2SO_4 or 0.0182 gram HCl.

In testing sodium or potassium bichromate, a convenient solution is made by weighing 5 grams of the salt and making a solution of 1 liter. This is almost tenth normal if the salt is pure or nearly so. (The commercial sodium bichromate in small crystals

Digitized by Google

now on the market is almost chemically pure.) Ten cc. of this solution are diluted to about 50, five cc. of HCl added, then 10 cc. of potassium iodide solution and the titration carried out as already described. Because of the great dilution used, it is well to make a number of titrations in this case, as an error of 0.1 cc. in titrating will cause an error of 0.5 per cent. in the determination.

The determination of Cr_2O_3 in chrome leather has been made in a number of ways. The method described in the article which follows is new to the writer, and it seems very desirable that as many members of the Association as possible should test it, and send in their results to the committee, so that when our report is made up some definite knowledge of the availability of this method may be at hand. Some tests have been made in this laboratory, and seem to indicate that the method is dependable. We have not succeeded so far, however, in getting sharp end-points in the titration. We are of the opinion that nickel crucibles and nickel or quartz tubes are not necessary. We have used a large porcelain crucible and a steel tube with satisfactory results. The writer of the article in question does not mention quantities of nitrate or of bicarbonate.

After experimenting with Mr. Tarshis' method, it occurred to the present writer that it ought to be possible to substitute some other salt for sodium nitrate, in order to avoid the production of nitrite, and thus make possible the ordinary titration of the Cr as bichromate in acid solution. Several trials were made with potassium chlorate, the mass being heated after the combustion was complete in order to convert the unused $KClO_3$ into KCl. Results have thus far been always much too high, probably owing to incomplete expulsion of the oxygen of the $KClO_3$.

Two methods are described in the "L. I. L. B." In the first, 0.5 gram of leather ash is fused with 3 grams or more of an equal mixture of K_2CO_3 and Na_2CO_3, converting the chrome and alumina into chromates and aluminates. When the melt is dissolved, if any considerable amount of material is insoluble, it is best to fuse this again, to insure against loss of Cr or Al. The alumina is precipitated by making the solution just alkaline with NH_3, and after filtration the solution containing the chro-

Digitized by Google

mates is treated as already described. It may be made up to 500 cc., and trial will show the proper amount to be titrated for Cr_2O_3.

This method is laborious, and if it is not necessary to determine magnesia the leather ash may be heated with about 5 times its weight of a mixture of equal parts MgO and Na_2CO_3. This mixture does not fuse, but at a bright red heat the Cr of the ash is readily converted into sodium chromate, and the time required is less than with the mixed carbonate. The cooled mass is dissolved in water and the solution of aluminate and chromate treated as above. This is the second method of the "L. I. L. B." Any process which will yield good results without previous ashing of the leather should be gladly welcomed.

ELK TANNING CO. LABORATORY,
Ridgway, Pa.

A RAPID AND DIRECT READING METHOD FOR CHROME ANALYSIS.[1]

By Ralph V. Tarshis.

At a leather research laboratory, much work has been done on Cr_2O_3 in leather. It was found by the writer that complete burning of the leather and the fusion of the ash with sodium carbonate was a long and tedious operation, especially when there were about twelve grams of leather taken for each analysis. From this problem was evolved a method that would give the Cr_2O_3 in less than fifteen minutes.

First it was found that the leather could be burned up and at the same time the chrome changed to sodium chromate in a few minutes by adding the leather to a fusion of sodium nitrate. This saved at least two or three hours igniting and fusing with sodium carbonate. In a nickel crucible about 1½ inches diameter and 1¾ inches deep was fused some sodium nitrate, and a quartz or nickel tube (1-inch diameter, 6 inches in length) was lowered into the fused sodium nitrate. This tube permitted the

[1] *Chemist-Analyst*, No. 9, pp. 5-6.

Digitized by Google

leather to be burned in a small crucible without any loss by spattering. The Bunsen burner flame was removed after the sodium nitrate was melted and the leather was then dropped into the tube in small amounts, waiting until each addition burned up before adding more; by this means it takes but a few minutes to burn large amounts. The tube is now raised out of the fusion, and after the fusion solidifies, it is dissolved in water. The end of the tube that was in the fusion is also placed in water in order to dissolve off the sodium chromate that is spattered on the inside wall of the tube. The solution is made up so that there is 100 cc. volume for each gram of leather or any other substance taken.

For example: 3.9425 grams should be made up to 394.25 cc. and 25.36 cc. of the made up solution is taken for analysis. This can be done by remarking a 25 cc. pipette to 25.36 cc. To this 25.36 cc. portion for titration is added 10 cc. of a tartar emetic solution (whose value for 10 cc. is known in terms 1/10 N. iodine), and some sodium bicarbonate added and then titrated at once with 1/10 N. iodine.

Subtracting the 1/10 N. iodine reading found with the 25.36 cc. portion from a blank reading of 10 cc. of the tartar emetic solution, the difference gives the per cent. of Cr_2O_3 in the sample. This method for titrating for sodium chromate is used instead of the method with 1/10 N. thiosulfate, because it does not necessitate an addition of acid. It was found that sodium nitrite ($NaNO_2$) was formed during the fusion and that the addition of an acid necessary for titrating with the thiosulphate would reduce the sodium chromate.

The eliminating of the sodium nitrite ($NaNO_2$) and the re-oxidizing to sodium chromate again caused much loss of time, all of which is entirely avoided by using the writer's method. The solution that was used for the leather analysis in the laboratory was 16 grams of crystal tartar emetic in one liter of water. The blank iodine value for 10 cc. once being obtained, does not have to be determined again. This method can be used with many other substances that contain chromium.

Brooklyn, N. Y.

Digitized by Google

NEW RESEARCHES ON THE APPLICATIONS OF ACTIVE ALUMINUM.—THE "ALUNGALLINES".[1]

By E. Kohn-Abrest.

In 1911 I published some results obtained by bringing active aluminum into contact with tanning solutions, infusions of bark, wood, etc. The following is the result of the most recent investigations:

Active aluminum brings about very easily the precipitation of tannin from its solutions and attempts have been made for a long time to fix the quantitative law of this precipitation. Formerly it was believed that one part aluminum precipitated five parts tannin; but in reality the settling power for tannin of the hydrates which are found when active aluminum is plunged into various liquors is much greater. Everything proceeds as if the precipitates of tannin and aluminum which form were mixtures of free aluminum more or less hydrated, and of a compound of tannin and aluminum containing very little aluminum.

Under the influence of prolonged contact, or what amounts to the same, mechanical agitation after removing the sheet of metal, the excess of free aluminum gradually takes possession of the tannin which is still in solution. It is understood that under these conditions it tends to disappear from the solution, which is gradually enriched in tannin without increasing the amount of active metal used. This is the reason it is sometimes best to take the sheets of aluminum from the solution before the tannin precipitates and to let the products of oxidation act alone. The hydrates obtained under these conditions possess analogous properties as far as tannin is concerned to the anhydrous oxides which Wislicenus obtained by the oxidation in damp air of grains of aluminum largely amalgamated. But the former method seems to give better and more practical results.

It is to be hoped that the amount of metal used can soon be reduced since the price of aluminum is high.

Action of active aluminum on vegetable infusions.—To repeat briefly the experiments made on infusions of oak bark with

[1] Bulletin des Chimistes de sucrerie et de distillerie, through LaHalle aux Cuirs, technical supplement No. 7, April 5, 1914. Translated for *J. A. L. C. A.*

Digitized by Google

active aluminum: 10 kilo oak bark was treated three times with 32 liters of water at 9°-12° C. for 24 hours each time. Three very much colored solutions were obtained which were successively treated with the same sheet of active aluminum several times. Each of the three sheets was 25 cm. by 34 cm. and weighed 330 g. Before using they were scoured with concentrated potash and made active by immersing for 1 minute in a solution of mercury bichloride. After draining and rinsing in water they were plunged into the solution of tannin, and remained there 18 hours. The liquid of the first infusion was entirely decolorized and free of tannin after three actions of the aluminum sheets. The second liquid was clarified and freed of tannin after five applications of the sheet. For the third only one was necessary. The bark infusions decolorize rather rapidly, become milky and, when the action is finished, that is when the hydrates formed no longer find any substance to combine with, the milky emulsion separates and the precipitate deposits like curds, in a perfectly colorless and clear liquid. In this case the loss of weight of the sheets was 125 g. and the precipitate recovered when vacuum dried was 1,300 grams. Attempts have been made to purify the product obtained, *i. e.*, to separate as much as possible the aluminum from the vegetable matter with which it is combined. After various trials by breaking the mass with HCl a product was obtained containing only 5.5 to 6 per cent. of aluminum.

Action on chestnut wood extract.—By the kindness of Messrs. Trillat and Ehrmann experiments were made on fresh chestnut wood extract at 40 Baumé, and also on the commercial extracts 3 liters of this were diluted with water to 9 liters and put in contact with a sheet of aluminum weighing 104.5 g. and having an area of 400 sq. cm. activated as described above. Two treatments caused the complete precipitation of tannin. The loss of weight of the sheet was 24 g. and the weight of the vacuum dried precipitate 180 g.

Attempts to prepare a tanning product.—The ease of freeing various infusions from vegetable substances led to the attempt to extract a part of the precipitates obtained. By treating with HCl and utilizing differences in solubility in its presence between

Digitized by Google

the tannin and the chloride of aluminum, it was possible to completely regain the tannin when it had been precipitated by the aluminum from a solution of pure tannin. Unfortunately such is not the case when the substance is accompanied by all the matter extracted from bark or wood. But the attempts made at separation have led to an interesting result. Among the products obtained when treating these organo-aluminum precipitates with HCl gas, there are some which merit special study. Analysis of one gives "Tannin" 33.1 per cent., water 34.05 per cent., aluminum 12.7 per cent. and chlorine 20.15 per cent. These solid substances, whose composition is very peculiar, rather like solutions of "Tannin" in a special hydrated aluminum chloride, possess very strange properties. They look like a yellowish powder, dry, without odor and largely soluble in water. The solution is acid and gives all the reaction of tannin, black violet color with perchloride of iron, fixation on hide powder, etc.

Alungallines.—If one uses SO_3 instead of HCl, the products are much more interesting, and more easily obtained. The dried precipitate is simply treated with H_2SO_4 more or less diluted. The substance obtained is dried until solid in a vacuum or on a water bath which is quite a rapid process. The acid should be in proportion to the aluminum contained in the tannin-aluminum compounds or to the quantity of ashes left by the precipitate. That should be enough to transform into sulphate of aluminum $(Al^2SO^4)^3$ a quantity of aluminum equal to that contained in the ashes of the tannin-aluminum precipitate. Because of their origin and composition, the products obtained by the action of acid on precipitates formed when active aluminum is brought into contact with liquids containing tannin or its like, have been named *alungallines*. Those formed by sulphuric acid particularly deserve the name because they contain all the constituents of sulphate of aluminum more or less dehydrated, and of tannin. They are likewise powdery substances more or less yellow and dry; like hydrochloric alungallines they are almost entirely soluble in water and give tannin reactions. These sulphuric alungallines when treated with solvents used for tannins give up the latter—especially when treated with acetone. The composition of one was aluminum 13.4 per cent., SO_3 30 per cent., tannin 37.62 per

Digitized by Google

cent., water 18.98 per cent. If precipitation or drying are done differently the composition is different. Alungallines may therefore contain much more tannin than the one above given. Alungallines may be used as chemical products, perhaps as tannins, or as coloring matter, as mordant, etc. Finally tannin, or at least tanning principles may be extracted from them. It is interesting to note that active aluminum will precipitate tannins from solution in whatever mixture or dilution, and that the tannin may be recovered from the alungallines formed during the operation. All the operations are simple and economical, and form an important use of active aluminum.

Encouraging results have been obtained by the author and M. Bouligand in treating the precipitation of tannin in all sorts of vegetable infusions. Experiments with the aluminum on alkaloid infusions were particularly interesting; first because many hydro-alcoholic solutions of alkaloids were shown to be decolorized by the active aluminum without noticeable loss of alkaloids; second because of the possibility of using the precipitates obtained at the time of purification (if the infusions contain tannin) for making alungallines, and on the other hand for extracting alkaloids left in the purified liquids.

Application of Active Aluminum to Estimation of Tannin.—Wislicenus proposed the use of hydrates or oxides obtained by exposing to air large grains of aluminum strongly amalgamated in the determination of tannins. He established the fact that hydrated and even the unhydrated oxide takes possession of the tannin. Likewise he noticed that vegetable substances generally accompanying the tannin in infusions of bark not absorbable by hide powder are not fixed by oxide of aluminum. He has drawn up the following process of determination of tannin:

Aluminum hydrate in large proportions (2 g. or 3 g. to 1 g. is added to the solution of tannin, allowed to stand 24 hours, aired and washed twice in water. The liquids aired are put together and evaporated to the former volume. Pipette a certain volume, and after evaporating at 100°, weigh the residue.

Evaporate under the same conditions a like amount of the original tanning solution. The difference in weight expresses

Digitized by Google

the proportion of tannin contained in the volume of liquid evaporated after the special Wislicenus treatment with aluminum hydrate. Following him further, one can use the anhydrous oxide coming from the hydrate calcined to red ("Tannalithe"). In this case air the precipitate after washing several times with water to gently remove extraneous substances, dry the precipitate at 100°, weigh it, ignite and weigh again. The loss gives the tannin.

After some modifications of the above we obtain the following which seems a suitable method:

Bring 100 cc. of a 0.5 per cent. to 1 per cent. solution of tannin into contact with a sheet of aluminum about 1 mm. thick and weighing about 3 g. This sheet has been made active by immersion for three minutes in a 19° aqueous solution of bichloride of mercury, and rinsing with water. Keep it in till all the tannin is precipitated, *i. e.,* till the liquid gives no color with perchloride of iron. In general this will take 4 to 5 hours, but with a mechanical agitation only one hour. If one activation of the metal is not enough take it out when the bubbles of hydrogen cease forming and make it active again as above. After the tannin is precipitated, proceed as Wislicenus directs above. If one desires very precise results it will be well to take account of the few milligrams of aluminum which are dissolved during the action of the active aluminum. To do this, after the evaporation at 100° and weighing the two residues, continue the operation by determining the ashes of each residue and baking from the weight of the extract at 100° which corresponds to the liquid treated the excess of weight of the ashes of this residue over the normal residue *i. e.,* liquid not treated with active aluminum). The correction is very small and not needed in general.

ABSTRACTS.

Anthrax Disinfection. G. Abt. August, 1913, *Bulletin of the Société d'Encouragement pour l'Industrie Nationale.* Anthrax disinfection has long been widely investigated but no method has been found which has stood the test of long usage. The Tanners' Congress of 1911 at Turin, ordered the investigation of two methods advanced at that time, the one

Digitized by Google

by Mr. Seymour-Jones, the other by Messrs. Schattenfroh and Kohnstein.

The number of cases of anthrax for the last few years is, in England 16 or 17, Germany 25 from 1898 to 1911 and about 40 from 1907 to 1911. In France the cases may be estimated at 40. This is really quite a small number when one considers how many hides are probably infected. Man is in fact very resistant to anthrax, and according to Mr. Daboust can be readily cured by serum.

However the disease can be stamped out only by sterilization of the infected hides. This is our problem, and it is necessary to find a method which will not only disinfect, but will do so without injury to the quality of the leather. We shall deal only with treatment of dry hides because investigation has shown that it is among them that anthrax infection occurs, not among wet, salted hides, and also that infected hides come in general from China, India, Malacca, Northern Africa, Argentina, Spain, Asiatic Turkey, the Balkan Peninsula, and sometimes from Russia and Hungary. Hides from these countries should certainly be subjected to treatment, especially since many of them are not designed for fine uses.

In seeking a method we realize that it is necessary to find one which will not spoil leather for definite uses, and which also harmonizes as far as possible with those already in use.

It is a difficult question to judge whether a process of disinfection can protect men from anthrax. In the first place, if one treats the anthrax spores with an antiseptic, although their injurious character may be lessened, one can never be sure that they are dead, and they are not harmless unless dead. On the other hand disinfection of the hides is rendered difficult by the proteid matter which lessens the effectiveness of most disinfectants. Two series of tests were therefore made, one on dried skins of guinea pigs known to have died of anthrax, and therefore surely containing the spores. These were disinfected and live animals inoculated with them as a test of success. The second series was made with dried spores on glass slides, and it was found that the accepted idea that antiseptics take a long time to act on anthrax spores is not true, in fact that they act very quickly, without increasing the strength. In working with the dry spores the usual method of suspending them in the disinfectant was not followed. The simple method of Chamberland and Fernbach was used—*viz.* drop from a hair pipette three drops of the suspension of spores on a slide lying in the bottom of an 8 cubic centimeter tube stopped with cotton, then dry it rapidly in a vacuum. To provide a layer which will oppose disinfection one may cover the slide after dessication, with horse serum and dry again. It is very easy to pick up these slides with sterilized pinchers, pass them through a wash and inoculate bouillon with them under perfect antisepsis.

The cultures were placed in a medium weak in peptone and after seven days contained nothing but spore bearing germs, except a few forms of involution. When heated on a water bath in sealed bulbs, containing

Digitized by Google

about ½ cubic centimeter, the resistance to 100° varied between large limits according to the strainage and number of generations. The most resistant stood 3½ minutes, the least from 10 to 1 second, subtracting the time necessary to raise the liquid to 100° within the bulb. This lime was calculated to be 10 seconds in the following way. Before sealing the bulb put in some large white crystals of a substance insoluble in water melting at about 100°. The substance used melted at 96°. When shut up in the bulb and plunged in boiling water the crystals melted in about 12 seconds.

All the strains used (see Table I) came from the Pasteur Institute except III which was isolated from a cattle epidemic in September, 1912, and two of Algerian anthrax sent by the institute of Algiers. It was included because it is very destructive to Algerian sheep, which however are resistant to European anthrax. Since we know that anthrax hides come from northern Africa it is well to know how this species acts toward disinfectants.

TABLE I.

No.	Generation	Age when used	Resistance to heat	Virulence	Indirect proofs
I	1	40 days	5 min. at 90°	Kills in 42 hrs. to 4 days	—
I	2	40 days	1 min. at 100°	Kills in 3½ days	—
I	3	42 days	5 min. at 90°	Kills in 60 hrs.	—
II	1	31 days	*a*. 1 min. at 100° *b*. 2 min. at 100°	Kills in 60 hrs. Kills in 3 days	— —
III	1	80 days	—	Kills in 60 to 40 hrs.	Virulent after 65 days
IV	1	48 days	—	Kills in 3½ days	Virulent after 65 days
IV	2	20 days	2 min. at 100°	Kills in 4 days	—
Algerian	—	32 days 35 days 35 days	—	Kills in 40 hrs. Kills in 60 hrs. Kills in 60 hrs.	Virlulent after 52 days

In working with hides containing anthrax one must have them dry. In this case skins of guinea pigs which had died after anthrax inoculation were used and it was proved as V. Esmarch says, that the spores form in the dark at 20°, 26°, 37° C. if the skin is not dried too rapidly nor so slowly so as to allow decay germs to displace the anthrax growth. The spores were visible in the middle of the rod-shaped anthrax bacteria in 24 hours but did not become free until after three or four days. The bacteria were still intact after 6 days at 37° but disappeared after 5 days at 20° and 27°. The spores formed in 50 hours. If exposed to the light

Digitized by Google

on the flesh side there is no sporulation. After three days characteristic bacilli were present but in 10 days had disappeared. If the hides could be dried in the sun immediately after flaying, it seems they would contain no spores. Certain it is that after 15 days exposure in the light anthrax can exist only as spores. It is generally admitted that oxygen is necessary to the formation of spores. They are found only near the surface while the bacilli have been observed by V. Esmarch as deep as the capillaries surrounding the sweat glands. An attempt was made to color the spores but with no sure success, because it was impossible to tell whether the things colored were anthrax spores or some other bacilli. Also it is *possible* for spores to form deep in the hide, so surface disinfection is not sufficient.

It is usual to show the presence of spores by warming the medium or object in which they are suspected. Weil says that all vegetative forms of anthrax bacillus are killed in 5½ minutes at 65°, in 4 minutes at 70°, 1 minute at 80°. This proof may be combined with the resistance experiment by putting a small piece of hide in a tube with sterilized water. Seal the tube and treat as the bulbs mentioned above. In this case, however, the increased volume (10 cc.) makes the time longer (40-45 seconds) until the crystals melt. After cooling take out the piece and put it in the bouillon.

Only two of the 8 skins used contained spores resisting 2 minutes at 100°. Anthrax could be isolated from the bouillon of 3 others after 1 minute at 100°, or 5 minutes at 90°.

Isolation did not succeed for the other 3, although they contained many other bacilli, so one cannot say anthrax was not present. The resistance of the spores in these skins was probably feeble. Hilgermann and Maumann give 2 minutes as the time for heating a guinea pig skin in steam, and Esmarch says some spores in some dried skins do not resist 100°. Further investigation would be valuable.

The hides which gave no cultures after heating were still virulent for guinea pigs after 52 to 130 days, perhaps because of imperfect sterilization. Three guinea pigs were inoculated from each skin and they all died of anthrax. *Methods of disinfection.* Besides mercury bichloride and HCl there are antiseptics which can kill anthrax spores, *viz*: the Halogen group; permanganate of potash 5 per cent; osmic acid 1 per cent (both in 24 hours) undiluted formic acid in 4 days; turpentine in 5 days concentrated ammonium hydrosulphide 5 days; ferric chloride 5 per cent., 6 days; arsenious acid 0.1 per cent., 10 days; silver nitrate 4.25 per cent., 8¾ hours; soda 4 per cent. and potash 5.6 per cent. 18 hours; oxygenated water 3 per cent., 1 hour; hydrofluoric acid 2 per cent., 2 hours. Study has been given to the halogens, permanganate of potash and the acids (except osmic). The others require such concentration and time as to be of no use. In fact the following are the only known ones presenting a chance of success.

Seymour-Jones Method.—Prepare a 1:5,000 solution of corrosive sublimate in an ordinary pit, with 1 per cent. formic acid for large and 0.2

Digitized by Google

per cent. to 0.3 per cent. for small skins After 24 to 48 hours put the hides in a saturated brine of NaCl for 1 hour, or salt by hand. Then they are like pickled hides and may be dried or kept wet. The exponents of this method say that the sublimate does not become fixed in the hide too rapidly at least in the presence of acid. It has been used by many with contradictory results, which will be referred to later.

A very energetic action on spores used to be attributed to corrosive sublimate. At 1:1,000 dilution it killed dry spores on silk threads in 1 to 30 minutes. But in 1890 it was shown (Geppert) that its antiseptic power was much weaker if the sublimate sticking to the spores was neutralized with a basic sulphide. A very high proportion of the sulphide (5 times that necessary to form mercuric sulphide) is necessary on account of some combination with the matter which constitutes the spore itself. Time also plays an important part, for it was found that spores treated with sublimate 1:4,000 to 1:500 for 24 hours, and then washed 5 minutes in sulphide of sodium 2:1,000 and 1:100 ($Na_2S + 9\ H_2O$ containing 32.5 per cent. Na_2S) did not grow in bouillon. But after 24 hours in the sulphide of sodium they grew. Thus it is seen that sublimate 1:5,000 cannot really kill anthrax spores. It is not worth while to study the results of sublimate on unneutralized spores since the results would be too varied, so we have merely investigated the influence of the following factors after partial neutralization. 1. Resistance of spores and "strain." 2. Addition of formic acid. 3. Presence of serum. 4. Proportion of formic acid. 5. Use of other acid. 6. Presence of salt. Ammonium hydrosulphide was freshly made in the laboratory and contained 0.41% NH_4HS. Two dilutions were used, approximately 2:1,000 and 16:1,000. The slides were in this 5 minutes, then washed 5 minutes in distilled water. The stronger concentration gave most rapid development of spores. No cultures were obtained from the weaker NH_4NS and three from the stronger, after ten seconds at 100° in 0.5 per cent formic acid. Resistance to temperature is analogous partially to resistance to sublimate. Algerian spores are killed by less concentration than European, the former by 1:5,000 to 1:3,000 in 1 minute, the latter by 1:5,000 in 1 to 3 minutes and one in 3,000 in 30 seconds.

When considering whether adding formic acid aids the action of the sublimate, or at least helps break up proteid combinations insoluble in mercury we remember that it was formerly thought that tartaric and hydrochloric acid (Krönig and Paul) diminished the action because decreasing the ionization of the Hg ion which is the main disinfectant. However, it has been shown, adding a soda salt helps the disinfecting power in spite of diminishing of the ionization, and formic and hydrochloric acid have been shown to have the same helpful action

To see whether the presence or absence of serum made any difference experiments were made on the same spores, some bare, some covered with serum, in the presence of acid. They were in general less resistant. Serum has the same effect as neutralization, *i. e.*, it makes higher con-

Digitized by Google

centration necessary to kill the spores. While addition of acid does not materially affect results it cannot be unfavorable. Too much must not be put in though for in a French tannery many hides were ruined by putting in 1 per cent. From 0.2 per cent. to 0.25 per cent. is enough to prevent the formation of insoluble mercury compounds. Since this is the case it makes no special difference what acid is used. Salt also dissolves the combinations of sublimate with proteids, but it hinders its disinfecting powers, because of the formation of a complex salt of Hg and Na. From 5 per cent. to 9 per cent. it is harmful whether with or without acid and serum or with acid alone. Therefore it cannot be used instead of acid.

These results cannot well be applied practically to hides because often during the whole course of tannage they do not become neutralized. A partial neutralization is after all most efficacious for disinfection.

The formic mercury method with sodium carbonate for neutralization (when it was done) has had good success. Neutralization with sulphide of sodium failed. With the concentration of the sublimate at 1:500 Sevcik succeeded in spite of the neutralization. If skins are neutralized they cannot be disinfected except when the spores are very weak, but in practice they are never neutralized except in sulphide limes. Hence our experiments were made without it.

None of the guinea pigs innoculated with these hides treated with bichloride and formic acid and not neutralized, died. The tests by culture showed all the hides but one free from anthrax although in the ones not kept sterile invading microbes might hide it. The results were on the whole satisfactory. In working on the slides the acid seemed to play little part so was left out in a few cases. In general this is not to be recommended for the acid is important for dampening and softening dry skins and for swelling them. Skins neutralized 24 hours with 2:1,000 sodium sulphide remained virulent, as also when a paste of lime and realgar was spread on the flesh side for 40 hours. A mixture of slaked lime and sodium sulphide 2:1,000 for 24 hours did not cause the spores to reappear; thus skins behave like slides in favorable cases, but may not be depended on to do so. Finally lime mixed with sulphide of arsenic did not neutralize the sublimate and even the cultures remained sterile. These experiments point to one conclusion, *viz*: that limes sharpened with arsenic are the least dangerous for dehairing skins sterilized with sublimate. The skins are not injured enough to cause serious loss. If the concentration of the formic acid is kept at 0.20 per cent. to 0.25 per cent. the conditions are the same as those recommended for softening dry skins, used in many tanneries. According to Parker hides thus softened gain 3 per cent in weight over those softened in ordinary soaks. It is a good plan to drum the hides in salt water and let them lie in it over night to remove the last of the sublimate which might cause grey stains. If the sublimate was as strong as 1:3,000 they might even then appear. Rather than use strong sublimate it would be better to prolong the process 48 hours. Experiments were made to see whether HCl could not be used more cheaply than formic acid. They are equally efficacious,

Digitized by Google

but HCl is considered more dangerous to the hides although it can be used in lower concentration. The price of the formic acid can be reduced, by using the baths over again, adding ¼ acid each time. To keep the walls of the pit from absorbing acid, paint them with boiled oil and then varnish. Disinfection with mercury in alkaline medium may be performed with oxycyanide of mercury, but it is not one-tenth as active as the bichloride. Finally, it is slightly more difficult to unhair skins disinfected by the Seymour-Jones method, than ordinary ones, but this is not an insurmountable difficulty, as the hides may be kept in the lime a few days longer.

Schattenfroh and Kohnstein's method.—This method proposed at the Congress of the Leather Industry at Turin in 1911, has been tried by various people. Results in killing the germs have varied from 10 hours, 2 per cent. HCl to 8¼ hours 3.65 per cent.—when a few still lived. With skins, sodium chloride added in sufficient quantity checks swelling and preserves the tissues from acid. Gegenbauer and Reichel fixed the minimum time for disinfection of spores on silk threads. They recommend 2 per cent. HCl (pure) and 10 per cent. NaCl for 48 hours at 15°-20°, or 1 per cent. HCl and 10 per cent. NaCl for 6 hours at 40°, and 10 liters of liquid to 1 kg. of dry skins. Criticisms is brought on this method because it damages the hides. It is like pickling which is used to make skins supple, therefore not for sole leather. Two per cent. HCl corresponds to 2.6 per cent. H_2SO_4. The harm becomes apparent only when the hide is depickled. This method will never be accepted for general use, but may perhaps be employed for those skins manifestly contaminated and threatened with destruction. If this method is compared with the sublimate method the latter seems to offer less risk, but safety rests entirely in the absence or insufficience of neutralization. Experiments have shown that no other acid is as satisfactory as HCl.

Disinfection with Chlorine.—Chlorine is the most powerful antiseptic and does not harm hides. Chloride of lime gives good results, containing a hypochlorite and free chlorine. The latter disinfects better than the former so was used in our experiments. The results of these gave the following principles for practice. It is a question whether 1:1,000, sufficient for guinea pig skins, is enough for large ones. Proteid certainly lessens the action. If the concentration is weak the action is very rapid. A great obstacle to the use of chlorine is the variable strength of hypochlorites and chloride of lime. The loss, the difficulty of obtaining exact strengths and of odor, do not recommend it except when others are rejected. Dr. Becker has recommended the use of oil of mustard dissolved in alcohol but it gives very poor results.

Conclusions.—After examining the different methods of disinfection it is evident that there is a great difference between methods suitable for hides manifestly contaminated, and treatment to be applied as a preventive to dry hides. In the second case the method of Seymour-Jones gave good results, provided unhairing was done with pure lime or lime

Digitized by Google

sharpened with arsenic sulphide; or with very concentrated sulphide of sodium. The Schattenfroh-Kohnstein method is rejected on account of its risks, both to the leather and by contagion. The use of chlorine seems impractical although experiments are lacking to show how it works on skins thicker than guinea pig. One cannot hope that these methods will entirely obviate death from anthrax, but if $^{9}/_{10}$ of the skins can be disinfected it is possible that deaths can be reduced to one or two for a country. As far as the Seymour-Jones method is concerned it may be remarked that the majority of cases of contagion occur among workers who handle the hides before liming. English statistics 1903-1909 show 60 cases in docks and ware houses, 11 indirect and 42 in tanneries, 13 of the latter were of workers among fresh hides, 13 were beamhouse workmen. Similar statistics come from Mazamet and St. Denis, which point even more definitely to contagion before unhairing. General disinfection should be tested for a year in a place where cases regularly occur, in order to prove it. It cannot be denied that the cost would be considerable. Seymour-Jones estimates it at $0.0074 *i. e.* 7+ mills per hide, by his process. This means 1 per cent. acid which is high, 0.02 per cent. being sufficient. For small skins it would be less, but for dry hides more, although the Seymour-Jones method is more economical than the others. He thinks the disinfecting should be done in the country from which the hides come. The slightly higher price which would be fixed by competition with salt hides would be compensated by safety of purchase, for dry hides can easily contain hidden defects. All this would necessitate a reform in the leather trade which would be difficult especially in a place like Mazamet where 57,572,000 kgm. of skins were used in 1912. If it is only a question of disinfecting suspected skins the Schattenfroh-Kohnstein method is best. The use of sublimate alone would be very risky, for the spores would be killed only in appearance. One might try a preliminary test followed by a control with chlorine 1.5 or 2:1,000. E. A B.

A New Clarifying and Decolorizing Agent for Tanning Extracts. Dr. Leopold Pollak. *Collegium*, No. 527; 129-30.—Since the article appearing in 1913 in *Collegium*, 517:84, the decolorizing agent mentioned there has become known as "edamin," vegetable blood, and has been used successfully as a substitute for blood in several extract works. Application has been made for a patent on the process and use so it is now possible to explain the material more in detail.

Edamin is made from soya beans. They are cleaned, freed from fats in a special mechanical way and, subjected to a process meant to enrich the nitrogenous substance and to remove the skins and the starchy parts. Thus edamin is better than other materials formerly recommended, such as oil cakes, bran and other residua, which contain an almost insoluble protein substance which naturally has practically no value for clarifying and decolorizing. The nitrogenous substance in the soya beans is similar to casein, (it is known that cheese is made from soya

Digitized by Google

beans in China and Japan) and it is this substance which is useful for clarifying and decolorizing. Many experiments have demonstrated that Edamin shaken up with water and used as an emulsion to clarify and decolorize gives very good results (see article mentioned above). Recent experiments have shown that it is well to let the watery emulsion stand 24 to 36 hours in a warm place, when mold causes decomposition and the solution becomes plainly sour and a white cheesy sediment forms.

If the solution is now used well mixed, when it looks like milk, to clarify and decolorize liquors containing tannin, the effect is greater when compared with former results.

A good method is to make up a 3 per cent. solution of edamin mixing with water at 35° C. and letting it stand 24-36 hours with occasional stirring.

Sooner or later, depending on the temperature of the air, one sees gas forming and may test the acidity with litmus. According to experiments explained elsewhere edamin forms in 24 hours about 5 per cent. lactic acid. When the solution begins to make the cheesy precipitate it is ready for use. The method is the same as with the usual blood clarifying. Into liquor cooled to 45° C. (113° F.) put a corresponding amount of edamin solution, stirring continually; raise the temperature to 65-70° C. (150°-160° F.) cool, and allow to precipitate. To obtain figures for comparison a like amount of edamin and blood must be used. The temperature, 65°-70° C., as well as the whole process of decolorizing is largely dependent on the kind of liquor. It is certain, for example, that French chestnut wood extract was easily clarified with edamin at 65° while Italian and Corsican liquors were not decolorized till 70°. Much depends on the quality of the wood. With the French liquors better results were obtained with edamin, with the Italian and Corsican like results, as also with oak wood liquors. It is often said that chestnut and oak wood extracts decolorized with blood are so popular because the lactic acid formed from the blood, is said to help the tanning. An extract treated with edamin as above contains at least as much lactic acid as when blood is used. Edamin will certainly find a wide use because the process is without odor and clean, even in warm weather. The method of manufacture of edamin, too, insures uniformity, while blood has very considerable differences in the amount of soluble albumin which naturally hinders the efficiency of the process.

E. A. B.

The Microscopical Examination of Skin and Leather Applied to the Study of Salt Stains. GEORGES ABT. *Bulletin de la Société d'Encouragement pour l'Industries Nationales Tome* 119. May 1913, pp. 646-666. *Collegium,* 1914, pp. 130-150.—The author gives an account in detail of suitable methods for "fixing" pieces of skin and leather previous to cutting sections and also suitable staining solutions for differentiating the important histological elements of the skin. A description is given of the structure of normal skin and the changes which take place therein in some of the

Digitized by Google

leather manufacturing processes as seen by examination of sections of skin at various stages. To explain and locate the origin of salt stains, sections of stained skin and leather have been examined.

The following solutions have been used for fixing:

1. Bohn's solution slightly modified.
   70 parts saturated solution of picric acid.
   10 parts formalin. (40 per cent.)
   1 part acetic acid.
2. 0.4 parts chromic acid.
   1.5 parts acetic acid.
   0.1 parts formaldehyde.
   100 parts water.

Both solutions gave good results. The skin was immersed for 24-48 hours. After dehydrating with two changes of absolute alcohol, the pieces were transferred for 1 hour to a mixture of toluene and chloroform (1:1), then in toluene for 1 to 1½ hours and lastly in a mixture of toluene and cedar wood oil (1:1) in which they were left overnight. They were then embedded in paraffin for cutting. The section should not be more than 0.01 mm. thick. Pieces of vegetable or chrome tanned leather are washed, then dehydrated without fixing and afterwawrds treated as above.

The following stains have been found useful:

For skin 1. Double coloration with saturated alcoholic solution of magenta diluted with 5 vols. water. The section is treated for 5-6 hours cold, or 1 hour at 37° C., with the magenta and then for 10-15 minutes with picro-indigo carmine made by tinting a saturated aqueous solution of picric acid with indigo-carmine as required. The section is then washed and treated with alcohol (90 per cent.) until no more color comes away.

2. Double coloration with haematoxylin (Heidenhains' method) and eosine.

3. 1 per cent. solution of safranine in 90 per cent. alcohol with same volume of water. Treat for 24 hours, and then differentiate with acid alcohol (HCl and abs. alcohol 1:1,000) following with abs. alcohol.

4 Phenolic thionine (saturated solution in 50 per cent. alcohol with 9 vols. water and phenol 1 part per 100). This stain is of little value if picric acid has been used for fixing.

For vegetable tanned leather: 1 and 2 similar to 1 and 3 above for skin.

3 Phenolic thionine for 20-30 minutes, differentiate with 1 per cent. acetic acid until clear then wash with 90 per cent. alcohol.

4. Aqueous solution of cotton blue, then treat with acetic acid and alcohol as in 3.

5. Methyl green for 15-20 minutes differentiating with 1 per cent. aq. tannin acid solution.

6. Iron alum solution (1 per cent.) for a few minutes for recognizing fibers impregnated with tannin.

For staining the elastic fibers: Weigerts fuchsine, orcein (0.4 parts

Digitized by Google

per 100 of 80 per cent. alcohol to equal or a less volume as required of 4 parts HCl per 100 of 80 per cent. alcohol).

For bacteria: Gram's stain may be used on leather and skin. For Gram-bacteria, thionine (with acetic acid washing) and magenta followed with picro-indigo carmine gave the best results.

For chrome tanned leather sections: Good results are obtained with picro-indigo carmine and especially with thionine and safranine followed with acid.

The appearance of the various histological elements in the skin is described in detail, from the skin in its normal state to the point where it decomposes and the hair begins to fall out. In these changes the connective and elastic tissues are little effected, the nuclei of the connective cells remain distinct in a well preserved skin but become rare as the skin decomposes.

Sections of sheep skins depilated with lime and arsenic sulphide were examined. The tissues were well preserved and the epidermis preserved nearly entire, the external and internal sheath of the hair was disintegrated. The outline and sometimes the nuclei of the cells in the sebaceous glands remian distinct. After liming the nuclei had disappeared.

The action of the puer is difficult to estimate and ought to be further studied. The acid bates and bran drench are thought to produce only a few changes whilst the action of dung is more vigorous.

The author has not noticed any alteration in the elastic fibers which retain the same affinity for stains after tannage. The connective tissues were swollen with lime so that the division into fibrils was not noticeable. After puering they return to the normal state and appear less compact than in the raw skin but the difference is not very marked. In the leather they are most distinctly separated from each other.

It is suggested that the examination of sections of skin in various stages might be used as a method of control in some of the processes of manufacture.

Salt stains: The work carried out in the question of salt stains is supplementary to and confirms the hypothesis deduced by the same writer from a chemical investigation of these stains (*Collegium*, 1912, pp. 388-408.)

Two distinctive types of salt stains have been recognized. The stains in the first class are distinguished by the presence of calcium phosphate in places where grains of calcium sulphate are deposited from the salt. In the section through these stains the nuclei of the connective tissue are very prominent and are proved to contain traces of iron and excess of tannin in stained leather. It is assumed that these nuclei have been protected from the destructive action of micro-organisms in the various processes by an envelope of an organic iron salt and of iron and calcium phosphate. The iron originates from the chromatin in the nuclei when it is proved to be present in traces, it also may originate from blood, the salt used to preserve the skin and form impurities in the skin. The

Digitized by Google

phosphorus acid is present in the nuclei. As the salt stain progresses the nuclei ultimately disappear, the connective tissues are disintegrated but not completely decomposed as they would be by the action of bacteria. It is remarked that bacteria were never found between the altered fibers and they appeared in no case to have entered the dermis.

The second stain examined applies only to horse skin and leather. It is characterized in the section by the presence of strongly pigmented epithelial tissues and absence of calcium phosphate. The connective tissues were nearly normal. Only those organisms which would penetrate with the tanning solution were found to be present. The writer assumes these stains to proceed from the brown pigment in the cells of the malpighi layer and external epithelial hair sheath in the original skin. The pigment is afterwards fixed by mineral matter so that decomposition in the limes etc. is resisted.

The presence of traces of iron is a common factor in the stains examined. The persistence of the connective elements, especially the nuclei and epithelial tissues is proved and the very slight changes that take place in the connective tissues lead the writer to conclude that bacteria play a very small part in the production of the stains he has examined so that he cannot accept the conclusions of Prof. H. Becker with respect to these particular stains.

The experiments and reactions from which the author has arrived at his conclusions are described in detail. Colored illustrations of sections of normal and stained skin and leather are given and also illustrations from photographs showing the appearance of salt stains on pelt and leather. J. T. J. in *Collegium.*

Modern Alum-Tanning (Weissgerberei). JOSEPH JETTMAR. *Ledertechn. Rundschau,* 6, 17-20, 25-30.—J. makes the following distinctions: (1) Pickling in the tanning of furs, which is identical with the pickling as ordinarily practised in tanning, and which is mainly practised on the pelts (Felle) of herbivorae; (2) Ordinary alum-tanning for the tanning of sheep, lamb and goat skins (without their wool); it is also practised in the tanning of the pelts of game or carnivorae; (3) Hungarian alum-tanning which was formerly used mainly for production of harness and saddlery-leather. The tanning of pelts (furs) has become a special branch of industry. The pelts are first soaked, then shaved on the flesh-side and tanned, finally cleaned from the hair-side. Pelts should be removed as quickly as possible from the animal, framed and air-dried. When the pelts are dried near a fire, a stove or in direct sunlight they agglutinate (verleimen) and the pelt is spoiled. Such agglutinated skins occur not unfrequently in game-skins that are used in ordinary tanning; the skins are said to be scorched (verbrannt). It is worse yet if the skins are only removed a long time after the animal's death or if not properly stretched (framed) or if they have been dried too long; in such cases putrefaction sets in, the skins are said to "stink." The so-called

Digitized by Google

sweating process of skins is a mild process of putrefaction which causes un-hairing. Sheep-pelts are sometimes green-salted and occasionally pelts of commerce are dry-salted. The pickling is done with salt and sulfuric acid; hydrochloric—formic—or lactic-acids however could equally well be used. The skins are also sowed with wheatbran and barley-grist, and cleaned with soap. In pickling with wheat-bran putrefaction must be guarded against by means of salt and by daily inspection (umlegen); too much salt causes depilation. The skins (pelts) after washing are dried by spreading (especially folds and claws) on floors first with the flesh-side uppermost, afterwards with the wool uppermost. In drying the skins shrink considerably. The flesh-side is finally rubbed with rye-flour; white wool is rubbed with chalk; this also concludes the furrier's work.

In common alum-tanning the hair is loosened by sweating (in case the hair is valuable); otherwise lime is used. The removal of lime is necessary afterwards if a stiff and brittle leather is to be avoided. Most of the lime is removed by mechanical operations and finally by pickling with wheat-bran in sour ferment. The hides are then tanned with alum and salt.

Thin skins can be dried in a few hours at 35° C.; with thicker skins the initial drying temperature should not exceed 25° C. and should never rise above 30° C.; if this caution is not observed a layer of salt forms on the outside, the skins show a "scab" (kraetzig). When the mechanical treatment of such leathers becomes difficult it is generally due to insufficient alum-tanning; this can be remedied by soaking again in alum. Determination of alumina and hide-substance gives a good indication in this case. Such alum-leathers receive a treatment with feather-white or China-clay.

Hungarian alum-tanning differs from the previous processes mainly by a treatment with melted ox-tallow; it only gives unsightly products and it not therefore practised any more, except in combination with chrome-tanning, when it produces very firm, durable and washable leathers. Alex F. Fuerst.

Tannin; Composition of. III. L. F. Iljin. *Ber.*, 1914, 47, 985-993. (See also this J., 1909, 665, 1151; 1910, 504.) By partial precipitation of a tannin solution with lead acetate, and extraction of the unprecipitated portion with ethyl acetate (Trimble, *The Tannins*, 1892, vol. I., 85), a product of higher rotatory power than the original tannin was obtained, whilst by decomposing the lead precipitate with hydrogen sulphide and extracting with ether, a product of lower rotatory power was obtained. By repeated fractionation in this way products of rotatory power $[\alpha]_D =$ about $+29°$ and $+117°$ respectively, were obtained. By similar fractional precipitation with zinc acetate, the zinc compound being decomposed by the calculated quantity of dilute sulphuric acid, products having $[\alpha]_D = +5.16°$ and $+137.85°$ respectively were obtained. The former was spar-

Digitized by Google

ingly but the latter readily soluble in cold water. The produce of higher rotatory power yielded gallic acid and dextrose on hydrolysis.

A. S. in J. S. C. D.

Tannin; Constitution of, XI. A. GEAKE and M. NIERENSTEIN. *Ber.*, 1914 47, 891-898. The formation of dextrose in the hydrolysis of tannin with acids (compare Fischer and Freudenberg, this J., 1912, 390) is confirmed. Nierenstein's earlier failure to detect dextrose as a component of the tannin molecule (this J., 1912, 502) was due to the use of alkali for effecting hydrolysis. The dextrose is not present in a free or loosely combined form: The rotatory power of tannin is not diminished by the action of beer yeast, as stated by Biddle and Kelley (this J., 1912, 433-40), provided care be taken to prevent infection by moulds (compare Knudson, J. S. C. I., 1913, 545). By partial hydrolysis (4 hours with 5 per cent. sulphuric acid) of carefully purified tannin, there were produced 2½-4 per cent. of a crystalline substance, not yet identified, which did not yield sugar on hydrolysis, 20-25 per cent. of gallic acid, and 60-70 per cent. of an amorphous substance of almost the same composition and properties as the original tannin, but differing from the latter and from the pentadigalloylglucose of Fischer and Freudenberg (*loc. cit.*) by its considerably higher rotatory power, especially in glacial acetic acid and in alcohol.

A. S. in J. S. C. D.

Exploitation of the Tanning Materials of Paraguay. J. FRONTANIELLA. *Bourse aux cuirs de Liege.* Jan. 4, 1914.—Paraguay has 14 plants containing high percentages of tannin, several of which are unknown in Europe. The abundance of quebracho and urunday, from both of which extracts are made for export, has caused manufacturers to neglect other materials of equally good quality, but yielding somewhat less tannin. Certain of these which grow along with the quebracho require much less complicated processes than that very hard wood, and a small addition to the extract factories, employing but few hands, would suffice to utilize them. No doubt there are among these materials, tannins which could be used to replace sumac, valonea, etc., which are constantly becoming more high-priced, but lack of technical knowledge in the countries where they grow has prevented their utilization. The plants alluded to, beside the well-known quebracho, are the "curupay" (*Piptadenia macrocarpa*), "urunday" (*Astronium urundeiva*), "ibira pyta" (*Peltophorum vojelianum*), "timbo" (*Enderlobium timbouva*), weeping willow, "ihvaporoitih," (*Eugenia Braziliensis*), "ihvahai pita," (*Eugenia* ———), "ihvihrapuihta" (*Peltophorum dubium*), "nangapireh," (*Eugenia* ———), "kurupaih-ra" (*Piptadenia rigida*), "inga" (*Inga affinus*), "caatigua-moroti" (*Trichilia Hieronymi*) and "pakuri" (*Rheedia Braziliensis.*)

The writer (who is a citizen of Paraguay, studying at the Liege tanning school) objects to a recently published statement in a paper on the quebracho industry by an English writer, that the supply of native labor

Digitized by Google

is scanty, and that the climate of Paraguay is not such as to be endured by foreigners. Figures are given to prove that the climate is both pleasant and healthful. In winter the temperature averages 53° F. and in summer from 79° to 89° F. L. B.

PATENTS.

Process of Treating Water. U. S. Patent 1,095,893. CLARENCE P. LANDRETH, Philadelphia. A process of precipitating matter from water by means of electricity, with aluminum electrodes.

Drying Japanned or Varnished Leather. U. S. Patent 1,095, 498. ALFRED GENTHE, Worms, Germany. The leather is exposed to a current of dry air in the presence of violet light and ultra-violet radiation.

Apparatus for Concentrating Liquors. U. S. Patent 1,090,628. PAUL KESTNER, Lille, France.

Leather Rolling Machine. U. S. Patent 1,090,433. CARL VOSS, Newark, N. J.

Method of Treating Hides before Tanning. U. S. Patent 1,091, 236. C. C. MOORE and W. FRANTOM, England. The use of chemically pure NaCl is the main point.

Leather-Working Machine. U. S. Patent 1,090,895. FRANK WAYLAND, Salem, Mass.

Artificial Leather. British Patent 28,210. L. LILIENFELD, Vienna. A textile fabric is coated with viscose or the like.

VACANCY AT THE TANNERS' INSTITUTE.

At the request of Dr. Allen Rogers we call attention to the fact that there is a vacancy in the teaching force of the tanning school at Pratt Institute. Any leather chemist who would consider such a position may learn particulars from Dr. Rogers, Pratt Institute, Brooklyn, N. Y.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. IX JULY, 1914 No. 7

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1914, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VEITCH, } . . . Past Presidents

OFFICERS, 1913-'14

PRESIDENT—W. K. ALSOP, Ridgway, Pa.

VICE-PRESIDENT—C. W. NORRIS, 80 South Street, New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y.

LLOYD BALDERSTON, Ridgway, Pa.

C. R. OBERFELL, Harrisonburg, Va.

T. A. FAUST, 323 Academy Street, Newark, N. J.

ELECTIONS.

ACTIVE

John F. Church, 121 Main St., Peabody, Mass.

Horatio A. Heller, Canton, N. C.

CHANGES OF ADDRESS.

Geo. W. Ellsworth, to 210 Second Ave., Dubois, Pa.

Walter Petrie, to % Hastings Tanning Co., Hastings, Ontario, Canada.

E. D. Van Tassel, Jr., to 12 Edgehill Road, Winchester, Mass.

V. Y. Shewade, to Box 151, Miller, Ind.

Digitized by Google

SYNTHESIS OF DEPSIDES, LICHEN-SUBSTANCES AND TANNINS.*

By Emil Fischer.[1]

Gentlemen: The substances mentioned in the title are ester-like derivatives of the phenol carbonic acids, to which belongs gallic acid, so widely distributed in the plant kingdom and discovered in 1786 by C. W. Scheele, as well as the famous remedy salicylic acid, and which, therefore, are interesting, not alone to chemists, but also to the plant physiologists and the medical profession. Their study occupies a large space in the history of the aromatic group, and it gives me pleasure to refer to the fact that, at no place, so much has been worked out concerning these substances as right here in Vienna. It suffices to recall the investigations of F. Rochleder, H. Hlasiwetz, L. Barth and recently of J. Herzig and his students.

These phenol carbonic acids possess, among other properties, the ability to form ester-like anhydrides with one another, in such a manner that the carboxyl of the first molecule unites with the phenol group of the second. As the simplest example, I would cite the first anhydride of hydroxybenzoic acid:

$$HO.C_6H_4.CO.O.C_6H_4.COOH$$

By similar coupling of a third molecule of hydroxybenzoic acid the following system results:

$$HO.C_6H_4.CO.O.C_6H_4.CO.O.C_6H_4.COOH$$

Such ester-like anhydrides, Freudenberg and I have named[2] "depsides." The word is derived from the Greek δέψειν (to tan), because many of these substances show resemblances to the tannins. According to the number of phenol carbonic acids which are coupled together, one distinguishes didepsides, tridepsides, tetradepsides. Thus the nomenclature is formulated as in

* Abstracts of this have already appeared in the JOURNAL, but we welcome the opportunity to republish the full text from the June number of the J. A. C. S.

[1] Address delivered before the Naturforscher-Versammlung, Vienna, Sept. 23, 1913; and published in *Ber.*, 46, 3253–89 (1913). Translated by Frank Rose Elder, Columbia University, and published in the *Journal of the American Chemical Society* through the courtesy and with the consent of Herr Fischer and of the editors of the *Berichte*.

[2] *Ann.*, 372, 35 (1910).

Digitized by Google

the case of the polysaccharides and polypeptides. Such depsides are nowise new, for the two substances just mentioned above, the di- and tridepsides of *p*-hydroxybenzoic acid, were obtained by Klepl in 1883[3] by simply heating *p*-hydroxybenzoic acid. But his simple procedure is not applicable to most of the other phenol carbonic acids, as they cannot stand the necessarily high temperature. Still older are the exhaustive investigations of Schiff,[4] on the formation of similar substances from the phenol carbonic acids by dehydrating agents.

By treatment of gallic acid with phosphorus oxychloride, Ch. Gerhardt,[5] in 1853, prepared the amorphous anhydride of salicylic acid from sodium salicylate, obtaining an amorphous product which showed the tannin reactions, and which he considered to be digallic acid, $C_{14}H_{10}O_9$. Prior to this, J. Löwe[6] had observed that gallic acid, when heated with arsenic acid, was changed into a tannin-like body. On repetition of the experiment, Schiff came to the conclusion that this product was also digallic acid. Later he and his students applied the anhydrization by phosphorus oxychloride to a whole series of other phenol carbonic acids, protocatechuic acid, salicylic acid, *m*-hydroxybenzoic, cresotinic acid, phloretic acid and pyrogallol carbonic acid. According to the conditions, didepsides or complicated anhydrides resulted.

Unfortunately, the majority of depsides described by Schiff are amorphous, and, therefore, have not withstood criticism concerning their individuality and composition. In particular, his view that the amorphous digallic acid is identical with tannin cannot be maintained.[7] This will be returned to later.

However, the procedure of Schiff, repeated in other hands, has led to sharply defined didepsides. Thus, in a patent of the firm of C. F. Böhringer and Son[8] is cited a useful process for

[3] *J. prakt. Chem.*,[2] 28, 208.

[4] *Ber.*, 4, 232, 967, (1871); *Ann.*, 170, 43 (1873); 163, 218, 219 (1872); 172, 356 (1874); *Ber.*, 15, 2588 (1882); *Gazz. chim. ital.*, 17, 552 (1887); *Ann.*, 252, 87 (1889).

[5] *Ann.*, 87, 159.

[6] *J.*, 1868, 559.

[7] Freda, *Gazz. chim. ital.*, 8, 9, 363 (1878); 9, 327 (1879); Bignelli, *Chem. Zentr.*, 1909, II, 1861–3; 1910, II, 23; cf. further the later history of the tannins.

[8] D. R. P., 211, 403; cf. *Chem. Zentr.*, 1909, II, 319, 1285.

Digitized by Google

preparing disalicylic acid with phosphorus oxychloride and I, together with Freudenberg, have shown that by the same treatment of *p*-hydroxybenzoic acid, under certain conditions, the didepside of the acid discovered by Klepl[9] is obtained in excellent yield.

Besides the depsides, which are true acids, the phenol carbonic acids also may form neutral anhydrides. To this class belongs the *p*-hydroxybenzoide $(C_7H_4O_2)_x$, of Klepl; then the different salicylides, cresotides, phloretides and probably also the tetra-*p*-hydroxybenzoide[10] of Schiff. These, however, cannot be further considered here.

The inducement to take up the synthesis of the depsides was presented by the following observation in the synthesis of polypeptides of tyrosine:

For the preparation of glycyltyrosylglycine, a chloride of chloroacetyl tyrosine was necessary. Since the free phenol group appears to hinder the action of phosphorus chloride, I thought of the scheme of protecting the latter by introducing a group which subsequently could be easily removed, and chose for this purpose the carbomethoxy group.[11] The application of this process to the common phenol carbonic acids is the starting point for all the products which I will take up to-day. I have, in this investigation, enjoyed the valuable assistance of different young professional colleagues, whose share is evident from the titles of the single publications, and of these I will mention particularly Mr. Karl Freudenberg.

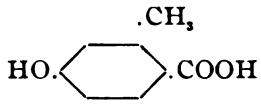
CARBOMETHOXYLATION OF THE PHENOLCARBONIC ACIDS.

Carboalkoxy derivatives of the common phenols have been long known. However, with a single exception,[12] which I will later mention particularly, these derivatives of their carbonic acids were lacking. It is now known that such substances result easily by the action of chlorocarbonic alkyl ester and alkali on phenol carbonic acids in cold aqueous solution.[13]

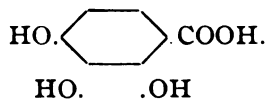
[9] *Ann.*, 372, 45 (1910).
[10] *Ber.*, 15, 2588 (1882).
[11] *Ibid.*, 41, 2860 (1908).
[12] Carboethoxy-salicylic acid of F. Hofmann.
[13] E. Fischer, *Ber.*, 41, 2875 (1908).

Digitized by Google

The course of the reaction is particularly smooth, if the phenol group is in the *meta* or *para* position to the carboxyl, and the accumulation of hydroxyl groups is no obstacle; for protocatechuic acid and gallic acid can be completely carbomethoxylated with slightly more than the theoretical quantity of chlorocarbonic methyl ester. The behavior is somewhat otherwise if a hydroxyl stands next to a carboxyl. Sometimes the complete carbomethoxylation succeeds in aqueous alkaline solution with an excess of chlorocarbonic methyl ester, as the case of orsellinic acid[14] and pyrogallolcarbonic acid,[15] demonstrates.

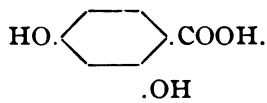


Orsellinic acid.



Pyrogallolcarbonic acid.

In other cases, under the same conditions, the ortho hydroxyl remains incompletely carbomethoxylated, even if a large excess of the reagent is employed. The case of β-resorcylic acid has been more minutely investigated.[16]



Salicylic acid behaves similarly. The complete carbomethoxylation of this latter acid can be attained by treatment with chlorocarbonic methyl ester in presence of dimethyl aniline in an indifferent solvent, for example, benzene. The process was first used by Fritz Hofmann for the preparation of carboethoxy salicylic acid, but has only been described in an American patent (No. 1,639,174* of Dec. 12, 1899), which has been recorded neither in the scientific nor in the collected chemical patent literature. I learned of it only by chance, in a private communication from Mr. A. Einhorn, just at a time when I was occupied in working out such a method myself. We have since applied the process with success, not alone to salicylic acid,[17] but also to some other

[14] E. Fischer and K. Hoesch, *Ann.*, 391, 366 (1912).
[15] E. Fischer and M. Rapaport, *Ber.*, 46, 2389 (1913).
[16] E. Fischer and K. Freudenberg, *Ann.*, 384, 234 (1911).
[17] *Ber.*, 42, 218 (1909).
* [This number is wrong: highest for June 30, 1914, 1,102,226. Ed.]

Digitized by Google

o-phenolcarbonic acids, such as the just mentioned β-resorcylic acid,[18] and the isomeric gentisic acid[19] (hydroquinone carbonic acid). Even with phloroglucine carbonic acid[20] which in aqueous alkaline solution takes on only one carbomethoxy group, the process succeeds if one uses a large excess of chlorocarbonic methyl ester and dimethyl aniline. However, the carboxyl group is also affected, and it forms an indifferent product, probably of anhydride-like nature. This, however, can be destroyed (as I, in conjunction with H. Strauss, have shown), by bicarbonate in acetone solution, without splitting off the carbomethoxy group. By this artifice, which is also applicable in other cases, the preparation of tricarbomethoxy phloroglucine carbonic acid,[21] succeeded without difficulty and thus it appears that the method is sufficiently complete to be available for all phenol carbonic acids.

It is remarkable that the difficulty encountered with the *ortho* phenol group disappears, if the carboxyl is not directly attached to the benzene nucleus; for *o*-coumaric acid (*o*-hydroxy cinnamic acid) can be very easily carbomethoxylated in aqueous alkaline solution. So far, the following acids have been completely carbomethoxylated:

(*a*) In aqueous alkaline solution:
- *p*-Hydroxybenzoic acid (*Ber.*, 41, 2877 (1908)).
- *m*-Hydroxybenzoic acid (will be published later).
- Vanillic acid (*Ann.*, 372, 47 (1910)).
- *o*-Coumaric acid (*Ber.*, 42, 226 (1909)).
- Phloretic acid (will be published later).
- Caffeic acid (will be published later).
- Ferulic acid (*Ann.*, 391, 357 (1912)).
- Protocatechuic acid (*Ber.*, 41, 2881 (1908)).
- α-Resorcylic acid (*Ber.*, 46, 1145 (1913)).
- Orsellinic acid (*Ann.*, 391, 366 (1912)).
- Gallic acid (*Ber.*, 41, 2882 (1908)).
- Pyrogallolcarbonic acid (*Ber.*, 46, 2390 (1913)).
- Syringic acid (will be published later).

(*b*) According to the process of F. Hofmann:
- Salicylic acid (*Ber.*, 42, 218 (1909)).
- α- and β-Hydroxynaphthoic acids (*Ann.*, 391, 352, 355 (1912)).
- β-Resorcylic acid (*Ber.*, 42, 225 (1909)).
- Gentisic acid (*Ber.*, 42, 223 (1909)).
- Phloroglucinecarbonic acid (*Ber.*, 46, 2400 (1913)).

[18] *Ibid.*, 42, 225 (1909).
[19] *Ibid.*, 42, 223 (1909).
[20] *Ann.*, 371, 306 (1910).
[21] E. Fischer and H. Strauss, *Ber.*, 46, 2400 (1913).

Digitized by Google

With the polyphenol carbonic acids, there is naturally the possibility of partial carbomethoxylation. They are governed by the orienting influence which the carboxyl exercises on the entrance of the carbomethoxy group. On this point the following data have, so far, been gathered:

In the *o*-, *p*-dihydroxybenzoic acid, the carbomethoxy group enters preferably in the *p*-position; and, if one decreases the quantity of chlorocarbonic ester to one mol, with gentisic acid,[22] *β*-resorcylic acid and orsellinic acid,[23] the *p*-monocarbomethoxy compound can be isolated in moderately pure condition.

It is otherwise with gallic acid; for here the first carbomethoxy group enters preferably in the *m*-position,[24] perhaps because the *p*-hydroxyl is protected from reaction by the two other neighboring hydroxyls. Partial carbomethoxylation succeeds easily with phloroglucinecarbonic acid; for in aqueous alkaline solution it takes on only one carbomethoxy group, and that happens most probably in the para position.[25]

The change from carbomethoxy compounds back to phenolcarbonic acids is accomplished with extraordinary ease by excess of cold aqueous alkali. Aqueous N ammonia acts similarly, though somewhat more slowly; but the carbomethoxy group is then split off mostly as urethane and not as carbonate. Neutral alkali carbonate also acts in the cold, but more slowly; while bicarbonate is rather indifferent, and thus, in most cases, serves to dissolve the acids. Only a few difficultly soluble alkali salts were encountered.

By insufficient quantity of alkali, partial elimination of the carbomethoxy groups results. Thus there was obtained from the dicarbomethoxyprotocatechuic acid, the *m*-monocarbomethoxy compound;[26] and from the tricarbomethoxygallic acid, the 3,5-dicarbomethoxy compound.[27] In both cases, preferably the *p*-carbomethoxy group was split off.

[24] *Ber.*, **42**, 222, 224, (1909).

[25] E. Fischer and K. Hoesch, *Ann.*, **391**, 364 (1912).

[26] E. Fischer and K. Freudenberg, *Ber.*, **45**, 2716 (1912).

[25] *Ann.*, **371**, 306 (1910).

[26] E. Fischer and K. Freudenberg, *Ibid.*, **384**, 235 (1911).

[27] E. Fischer, *Ber.*, **41**, 2885 (1908); further, E. Fischer and K. Freudenberg, *Ann.*, **384**, 240 (1911); cf. E. Fischer and O. Pfeffer, *Ibid.*, **389**, 211-4 (1912).

Digitized by Google

These partially carbomethoxylated substances have played a role in the synthesis of didepsides which will be spoken of later.

Furthermore, they can be methylated by diazomethane, whereby the carboxyl is esterified and all the free phenol groups methylated. These esters then yield, by double saponification, the corresponding partially methylated phenolcarbonic acids. In such a way, the structure of the monocarbomethoxyprotocatechuic acid,[28] and of the 3,5-dicarbomethoxygallic acid,[29] was determined.

The same process is also adapted to the practical preparation of such partially methylated substances as are difficult to prepare in other ways. In this manner, the *o*-methyl ethers of gentisic acid,[30] *β*-resorcylic acid[30] and orsellinic acid[31] were prepared; as well as the *o,o*-dimethyl ether of phloroglucinecarbonic acid,[30] the *p*-methyl ether[30] and the *m,p*-dimethyl ether of gallic acid.[32]

It is worth noticing that with the above-mentioned esters of carbomethoxylated phenolcarbonic acids, the ester group is removed more easily by cold concentrated sulphuric acid, the carbomethoxy group on the other hand more easily by cold alkali.

CHLORIDES OF THE CARBOMETHOXYPHENOLCARBONIC ACIDS.

These result from the action of phosphorus pentachloride on the acids, are usually crystalline, and show the important reactions of benzoyl chloride. Since, further, the carbomethoxy group can be subsequently easily removed, they have been valuable materials for synthesis.

It would naturally be still simpler to use in their place the chlorides of the phenolcarbonic acids themselves, but their preparation involves difficulties. In the action of phosphorus pentachloride it is well known that, besides the carboxyl, the phenol group is attacked, as R. Anschütz has shown in many cases. Only when the hydroxyl is crowded in between a neighboring carboxyl and a second *o*-substituent, is it removed from the action of phosphorus chloride and thus permits the preparation of the simple acid chloride.[33]

[28] E. Fischer and K. Freudenberg, *Ibid.*, 384, 236 (1911).
[29] E. Fischer and O. Pfeffer, *Ibid.*, 389, 199 (1912).
[30] *Ibid.*, 389, 199 ff. (1912).
[31] E. Fischer and K. Hoesch, *Ibid.*, 391, 372 (1912).
[32] E. Fischer and K. Freudenberg, *Ber.*, 45, 2717 (1912).
[33] Anschütz, *Ber.*, 30, 221 (1897).

Digitized by Google

The chlorides of the phenolcarbonic acids can, as a rule, be prepared, directly according to the method of H. Meyer,[34] by heating with thionyl chloride; but the products are with few exceptions oils, whose individuality appears doubtful to me, and from which the discoverer, aside from the esters, has prepared no other derivatives of the phenolcarbonic acids. Thus they cannot be compared in regard to usefulness, with the well behaved and relatively stable chlorides of the carbomethoxy phenol-carbonic acids. The process of Meyer has recently been improved by Kopetschni and Karzag, in that, in the place of the free acid, the alkali salt is treated with thionyl chloride. In this way they succeeded in obtaining a crystalline salicylic acid chloride.[35]

Finally, the chlorides of the completely methylated or acetylated phenolcarbonic acids have been long known. They are sufficiently stable to be of service in synthesis. But, the later removal of the methyl or acetyl group demands energetic treatment with acids or alkalies, and is thus excluded for all products which, by this treatment, undergo further change, for example, with the ester-like derivatives of the phenolcarbonic acids.

The chlorides of all the above-mentioned carbomethoxylated phenolcarbonic acids have been prepared by use of phosphorus pentachloride, either by gentle heating, or, in the case of sensitive substances, by shaking the acid and pentachloride with dry chloroform. If the chloride crystallizes with difficulty, it is advisable to remove the phosphorus oxychloride by dilution of the chloroform solution and by long, very gentle, heating of the residue in a high vacuum.

Most of the chlorides were obtained crystalline, only the tricarbomethoxy phloroglucinecarbonic acid, carbomethoxysalicylic acid, and carbomethoxyphloretic acid have so far remained as oils. The last two, however, can be sufficiently purified by distillation in a high vacuum.

These chlorides have been used, so far, for the following syntheses:

1. With alcohols they immediately form esters, which, by subsequent saponification with alkali, are changed into the ester of the

[34] *Monatsh*, 22, 415 (1901).
[35] *Chem. Zentr.*, 1913, II, 728.

Digitized by Google

free phenolcarbonic acid. An example is the preparation of ethyl gallate.[36] The method, naturally, has here no practical significance, because the esterification of the phenolcarbonic acids with the monohydric alcohols is attained much more conveniently by older methods. On the other hand the process acquires great importance in its application to the polyhydric alcohols and especially in the sugar series. This will be fully considered later.

2. The chlorides act energetically on the esters of amino acids and can be coupled with amino acids in aqueous alkaline solution. By subsequent splitting off of the carbomethoxy group there results finally the derivative of the phenolcarbonic acid. As an example, the synthesis of *p*-hydroxyhippuric acid (*p*-hydroxybenzuric acid)[37] may serve. It is accomplished according to the following equations:

$$CH_3CO_2.O.C_6H_4.CO.Cl + 2NH_2.CH_2\,CO_2C_2H_5 =$$
$$CH_3CO_2.OC_6H_4.CO.NH.CH_2\,CO_2C_2H_5 + HCl.NH_2.CH_2\,CO_2C_2H_5$$
$$CH_3CO_2.O.C_6H_4\,CO.NH.CH_2CO_2C_2H_5 + 3NaOH =$$
$$HO.C_6H_4.CO.NH.CH_2COONa + Na_2CO_3 + C_2H_6O + CH_4O.$$

Similarly, the isomeric salicyluric acid was prepared.[38] The process appears to me, to be much better than the one used somewhat earlier by Bondi[39] for the preparation of salicyluric acid from glycocoll and salicylic acid azide. Finally, there is still to be mentioned the synthesis of 3,4-dihydroxyhippuric acid from the chloride of the dicarbomethoxyprotocatechuic acid and glycocoll ester,[40] as well as of vanilloylglycine from the chloride of carbomethoxyvanillic acid.[41] I do not doubt that this method is sufficient for the preparation of numerous combinations of this sort.

3. Under the influence of aluminium chloride, the chlorides unite easily with benzene, and on subsequent splitting off of the carbomethoxy group, there result the unsymmetrical hydroxy

[36] *Ber.*, **42**, 1022 (1909).

[37] *Ibid.*, **41**, 2880 (1908).

[38] *Ibid.*, **42**, 219 (1909).

[39] *Z. physiol. chem.*, **52**, 170 (1907).

[40] T. Kametaka, *Ber.*, **42**, 1482 (1909).

[41] E. Fischer and K. Freudenberg, *Ann.*, **372**, 66 (1910).

Digitized by Google

derivatives of benzophenone. For *p*-hydroxybenzophenone,[42] the synthesis runs according to the following equations:

$$CH_3CO_2.O.C_6H_4.CO.Cl + C_6H_6 = CH_3CO_2.O.C_6H_4.CO.C_6H_5 + HCl$$

$$CH_3CO_2.O.C_6H_4.CO.C_6H_5 + 3NaOH = Na_2CO_3 + CH_3OH + H_2O + NaO.C_6H_4.CO.C_6H_5.$$

In this manner, there was prepared from α-resorcylic acid the 3,5-dihydroxybenzophenone,[43] from gallic acid the 3,4,5-trihydroxybenzophenone,[44] and from β-resorcylic acid the already known 2,4-dihydroxybenzophenone.[45] Finally, pyrogallolcarbonic acid gave the isomeric, 2,3,4-trihydroxybenzophenone,[46] which is identical with the mordant dye-stuff known under the name of alizarin yellow A, and thus its structure is established beyond doubt.

4. The chlorides can be coupled with the free phenolcarbonic acids and, by subsequent splitting off of the carbomethoxy group, didepsides obtained. By repetition of the operation, tri- and tetradepsides were prepared. The process is susceptible of many variations, as the following sections will show.

The applicability of the chlorides for synthesis is certainly not exhausted by these reactions. One can hope that they will be useful in most cases where benzoyl chloride and its derivatives have already proven themselves of service, and where it is desired to regain the phenol group by very mild hydrolysis. Thus, I believe without hesitation, that the chloride of carbomethoxy ferulic acid can be recommended for the experiment on the building up of curcumin, just as V. Lampe and J. Milobedzka[47] have succeeded in preparing the similar dicinnamoylmethane.

DIDEPSIDES.

Their history has been so adequately treated before that I must here content myself by describing only the new method. *p*-Hydroxybenzoic acid serves for the simplest case of the synthesis.

[42] *Ber.*, **42**, 1017 (1909).
[43] E. Fischer and H. O. L. Fischer, *Ber.*, **46**, 1147 (1913).
[44] *Ibid.*, **42**, 1018 (1909).
[45] *Ann.*, **371**, 317 (1910).
[46] E. Fischer and M. Rapaport, *Ber.*, **46**, 2393, (1913).
[47] *Ber.*, **46**, 2235 (1913).

Digitized by Google

The chloride of its carbomethoxy derivative unites with *p*-hydroxybenzoic acid in cold, aqueous alkaline solution, according to the following equations, and there results the alkali salt of carbomethoxy-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid:[48]

$$CH_3CO_2.O.C_6H_4.CO.Cl + NaO.C_6H_4.COONa = NaCl + CH_3CO_2.O.C_6H_4.CO.O.C_6H_4.CO_2Na.$$

On account of its slight solubility, it separates from its aqueous solution as the crystalline salt, but can be easily changed to the free acid by cold hydrochloric acid. In most other cases, the alkali salts are easily soluble in water and the resulting aqueous liquid is precipitated directly by mineral acid.

Since the chlorides used are ordinarily solid and in this form react too slowly, I, at first, used ethereal solutions for this coupling; later, acetone solution[49] was shown to be preferable in the majority of cases, and many couplings can be carried out satisfactorily only by use of this expedient. The ordinary procedure is as follows: The phenolcarbonic acid to be coupled is dissolved in the calculated quantity of *N* or 2 *N* alkali, some acetone added, the whole cooled to a low temperature and to this solution is added, in several alternate portions, another 1.1 mol of 2 *N* alkali and a solution of the chloride in dry acetone, the mixture being well stirred. The coupling takes place very quickly and completely even at low temperature. In most cases, the difficultly soluble coupled product can be precipitated by acidification and dilution with water. In other cases, the acetone is distilled off at low pressure, or the liquid is extracted with ether directly after acidification and dilution.

Instead of the alkali, dimethyl aniline can be used as the base, and the coupling can be carried out with exclusion of water. An example of this sort is found in the preparation of carbomethoxy-β-hydroxynaphthoyl-β-hydroxynaphthoic acid[50] from β-hydroxynaphthoic acid and the chloride of its carbomethoxy derivative. The coupling is effected by dimethyl aniline in benzene solution.

Finally, as a curiosity, may be mentioned the coupling of carbomethoxyferuloylchloride with *p*-hydroxybenzoic acid by several

[48] *Ibid.*, **42**, 216 (1909).
[49] E. Fischer and K. Hoesch, *Ann.*, **391**, 348 (1912).
[50] *Ibid.*, **391**, 355 (1912).

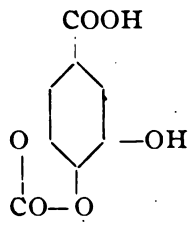
Digitized by Google

hours' heating of its solution in acetylene tetrachloride at 110°. The reaction is completed with evolution of hydrochloric acid gas.[51]

The general process, naturally, can also serve for the preparation of mixed forms and it may be mentioned historically that the first coupling of this sort was carried out with *p*-hydroxybenzoic acid, and the chloride of tricarbomethoxygallic acid, whereby the tricarbomethoxygalloyl-*p*-hydroxybenzoic acid resulted.[52]

If the phenolcarbonic acid contains only one hydroxyl group, the course of the reaction is simple. The behavior is naturally more complicated when 2 or 3 hydroxyl groups are present; for not only can isomeric carbomethoxylated didepsides result, but also complicated products, such as derivatives of tri- or tetradepsides. In most investigations which have been carried out in this direction, the product was a mixture whose resolution into its constituents presented difficulty. Only one example was worked out satisfactorily with definite results. This is the coupling of the dicarbomethoxyorsellinic chloride with orsellinic acid,[53] which was necessary for the synthesis of lecanoric acid.

In other cases, it has been preferable to protect a part of the phenol groups of the phenolcarbonic acids to be coupled, by carbomethoxy groups. As an example, the synthesis of digallic acid serves. Here the chloride of tricarbomethoxygallic acid was coupled, not with free gallic acid, but, with its dicarbomethoxy derivative in alkaline solution,[54] and if, instead of the dicarbomethoxy compound, the carbonylogallic acid[55] which contained a



[51] *Ibid.*, **391**, 359 (1912).

[52] *Ber.*, **41**, 2888 (1908).

[53] E. Fischer and H. O. L. Fischer, *Ber.*, **46**, 1138 (1913).

[54] E. Fischer, *Ibid.*, **41**, 2890 (1908); E. Fischer and K. Freudenberg, *Ann.*, **384**, 242 (1911).

[55] E. Fischer and K. Freudenberg, *Ber.*, **46**, 1120 (1913).

Digitized by Google

free hydroxyl in the *m*-position,[56] was used, still better results were obtained.

Another example is the coupling of dicarbomethoxyprotocatechuic acid chloride with monocarbomethoxyprotocatechuic acid in alkaline solution to give diprotocatechuic acid.[57]

According to the former process, in the coupling of a chloride to an *o*-phenol group in alkaline solution, a certain deviation which noticeably decreased the yield was observed, and thus, in many cases, it was impossible to isolate the product. Hence, another modification besides the use of dimethyl aniline was sought.

A satisfactory result was obtained when, instead of the phenolcarbonic acid, the aldehyde was used. The best example of this is furnished by the synthesis of *o*-diorsellinic acid,[58] for which the chloride of dicarbomethoxyorsellinic acid was brought together with *p*-monocarbomethoxyorcyl aldehyde in alkaline solution. The coupled product results in good yield and can be changed easily into tricarbomethoxy-*o*-diorsellinic acid by oxidation with permanganate. I am convinced that equally good results would be obtained with salicylic acid and similar substances.

For the preparation of *o*-didepsides the treatment of *o*-phenolcarbonic acids with phosphorus pentachloride and dimethyl aniline also serves, as is proven by the synthesis of disalicylic acid according to the patent of Böhringer and Son. We have applied the process with success to the monocarbomethoxy derivatives of gentisic acid and β-resorcylic acid, which contain the carbomethoxy group in the *p*-position. In both cases, the coupled product, *i. e.*, the dicarbomethoxy compound of the didepside, could be obtained crystalline.[59]

The carbomethoxy derivatives of the didepsides are as a rule crystalline substances. An exception is the amorphous derivative of digallic acid, which, so far, has resisted all attempts to crystallize it. Also, in other cases (for example with protocatechuic acid), we have given up the isolation of the carbomethoxy derivative, since the didepside itself is more easily purified. The

[56] *Ibid.*, **46**, 1124 (1913).

[57] E. Fischer and K. Freudenberg, *Ann.*, **384**, 238 (1911).

[58] E. Fischer and H. O. L. Fischer, *Sitzungsber. d. Berliner Akad.*, 1913, 507.

[59] E. Fischer and K. Freudenberg *Ann.*, **384**. 225 (1911)

Digitized by Google

carbomethoxy compounds are true acids and thus decompose alkali bicarbonate and, in general, are easily soluble in dilute potassium bicarbonate solution. This property can be used to advantage as a test of purity and also for separation from other indifferent substances.

The formation of the carbomethoxy didepsides often occurs with nearly theoretical yield. In other cases, this is lowered by side reactions. If the coupling takes place in aqueous alkaline solution, a large part of the chloride can be recovered as the corresponding acid. If the coupling takes place in alkaline acetone solution or in benzene solution with dimethyl aniline, there is obtained a varying quantity of indifferent substances of the nature of acid anhydrides. Their separation is carried out, as above mentioned, by treatment of the crude product with a dilute solution of potassium bicarbonate. Thus it is preferable to dissolve the crude product in a little acetone and then mix with the bicarbonate solution. The carbomethoxydidepside is then later precipitated from the aqueous solution of its potassium salt by mineral acid.

ELIMINATION OF THE CARBOMETHOXY GROUP.

As already mentioned, this can be carried out by cold dilute alkali or by aqueous ammonia. In the first case the alkali carbonate results, in the second, a large part of the carbomethoxy group is split off as urethane.[60] If the depside union is strong enough to resist the action of the alkali for hours then this procedure is best. For this purpose, the carbomethoxy derivative is dissolved in enough *N* alkali to neutralize the carboxy group, and to eliminate the carbomethoxy group a further 2 mols of sodium hydroxide are added. This operation is best carried out at 20° and the reaction is generally ended in ½ to ¾ hour. Only in the preparation of lecanoric acid from it carbomethoxy derivative was the alkali allowed to act for 2 hours, as lecanoric acid itself is very stable towards cold alkali; while with most didepsides, 24 hours' standing with 3 mols excess of *N* sodium hydroxide completely, or largely, splits the compounds into its components.

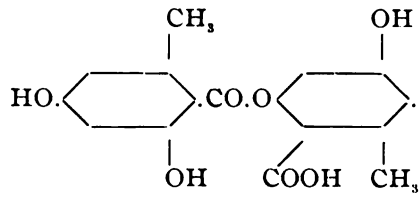
On account of this sensitiveness towards alkali, aqueous am-

[60] *Ber.* 41, 2885 (1908).

Digitized by Google

monia was used in the majority of cases for splitting the carbomethoxy derivative. Here, also, the action takes place best at 20° and N or $N/2$ solution in large excess was used. Since some of the ammonium salts of the carbomethoxy didepsides are rather insoluble in water, it is preferable, in such cases, to use acetone or pyridine as solvent.

The didepsides so far investigated are crystalline substances, difficultly soluble in cold water, which melt with decomposition, react acid and dissolve in bicarbonate solution. On account of the free hydroxyl group, they give colorations with ferric chloride which are suggestive of those produced by the free phenolcarbonic acids. If, for example, the phenol group is next to a carboxyl then, similarly to salicylic acid, a strong red to blue-violet coloration is observed. This color may not appear, however, if an hydroxyl is next to a depside union, for *p*-diorsellinic acid gives no real purple coloration.



All depsides are split into their components by excess of dilute alkali at room temperature, the reaction velocities differing very greatly.

By diazomethane, the depsides are totally methylated. Esterification of the carboxyl group takes place first and then methylation of the free phenol groups; the hydroxyl next to a carboxyl is attacked most slowly. The resulting, totally methylated, esters are beautifully crystalline substances which melt lower than the depsides and without decomposition. They thus serve very well as a means of characterization and identification of the depsides. As examples, I would cite the products which will be discussed later, namely, the methyl ester of trimethyl-*p*-diorsellinic acid from lecanoric and evernic acids and the pentamethyl-*m*-digallic acid from *m*-digallic acid.[61] If the depsides contain several adjacent phenol groups, as in gallic acid or pyrogallol carbonic acid,

[61] E. Fischer and K. Freudenberg, *Ber.*, **46**, 1127 (1913).

Digitized by Google

they are very sensitive to oxygen in alkaline solution, which deserves attention during their preparation.

The didepsides of gallic, protocatechuic, gentisic and β-resorcylic acids are precipitated by dilute glue solution and give precipitates with quinine acetate or by high dilution. They differ in this respect from the corresponding phenolcarbonic acids and approach the tannins.

TRIDEPSIDES.[62]

From monophenol carbonic acids, the theory only admits of the following type of tridepside:

$$HO.C_6H_4.CO.O.C_6H_4.CO.O.C_6H_4.COOH.$$

If, however, a di- or triphenolcarbonic acid is considered, then the following type is possible:

$$\begin{matrix} HO.C_6H_4.CO.O \\ HO.C_6H_4.CO\ O \end{matrix}\!\!\rangle C_6H_3.COOH.$$

Compounds of the second type have not been fully investigated so far. Perhaps to this class belongs a substance which Freudenberg and I[63] obtained as a by-product after saponification subsequent to the action of tricarbomethoxygalloyl chloride on gallic acid in alkaline solution. Our feeling that it is a bisgalloylgallic acid still lacks proof, however, and thus the exact description of our investigation has been delayed. Of the compounds of the first type, two examples are known, the di-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid, and the mixed form vanilloyl-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid,

$$\begin{matrix} OH \\ CH_3O \end{matrix}\!\!\rangle C_6H_3.CO.O.C_6H_4.CO.O.C_6H_4COOH.$$

The first was obtained by Klepl, along with the didepside, by heating *p*-hydroxybenzoic acid. Freudenberg and I prepared it in beautifully crystalline and apparently pure condition by the new method in the following way:

p-Carboethoxybenzoyl chloride was coupled with *p*-hydroxybenzoyl-*p*-hydroxybenzoic acid in alkaline solution. To split off the carboethoxy group, the product was dissolved in a mixture

[62] E. Fischer and K. Freudenberg, *Ann.*, **372**, 32 (1910).

[63] *Ber.*, **45**, 2712 (1912).

Digitized by Google

of acetone and pyridine and ammonia was then added. The tridepside could be obtained in moderately long needles by recrystallization from acetone, while Klepl has described it as a scarcely crystalline powder. In spite of this, we believe that his preparation is identical with our tridepside. The same product could undoubtedly be obtained in a third way, namely by coupling *p*-hydroxybenzoic acid with the chloride of carbomethoxy-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid.

The second mixed tridepside was prepared in an analogous way from carbomethoxyvanilloyl chloride and *p*-hydroxybenzoyl-*p*-hydroxybenzoic acid.

The two tridepsides melt above 200°, are practically insoluble in water and difficultly soluble in most organic solvents. With ferric chloride they give colorations in alcohol solution similar to that of *p*-hydroxybenzoic acid.

TETRADEPSIDES.[64]

Here also two forms are known, the tri-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid,

$$HO.C_6H_4.CO.O.C_6H_4.CO.O.C_6H_4.CO.O.C_6H_4.COOH,$$

and vanilloyl-di-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid,

The first was prepared from carboethoxy-*p*-hydroxybenzoyl-*p*-hydroxybenzoyl chloride and *p*-hydroxybenzoyl-*p*-hydroxybenzoic acid in alkaline solution. For the preparation of the second, carbomethoxyvanilloyl-*p*-hydroxybenzoyl chloride and *p*-hydroxybenzoyl-*p*-hydroxybenzoic acid served.

Here, all operations were rendered difficult by the slight solubility and reactivity of the materials. Both tetradepsides could be obtained crystalline. They are very difficultly soluble in most organic solvents and melt with decomposition.

Under the name of tetra-*p*-oxybenzoide, H. Schiff[65] has described a product that resulted by heating *p*-hydroxybenzoic acid with phosphorus oxychloride, and which has the same composition as the above tetradepside.

[64] E. Fischer and K. Freudenberg, *Ann.*, 372, 32 (1910).

[65] *Ber.*, 15, 2588 (1882).

Digitized by Google

A repetition of Schiff's experiment has shown that this preparation differs from ours and, thus, we do not believe it can be considered an ordinary polydepside.

Further application of the process to the synthesis of higher depsides has been abandoned on account of the increasing experimental difficulties and because the knowledge of such forms would seem to present no further great interest.

In conclusion I append the following list of depsides prepared by us. The earlier known substances, either artificially prepared or found in nature are designated by an asterisk (*). Those marked by † will be described shortly.

DIDEPSIDES.

*Di-*p*-hydroxybenzoic acid (*Ber.*, 42, 217 (1909)).
Di-*m*-hydroxybenzoic acid†.
*Di-salicylic acid (Salicylo-salicylic acid of Böhringer and Son).
Di-protocatechuic acid (*Ann.*, 384, 238).
Di-gentisic acid (*Ann*, 384, 230).
Di-β-resorcylic acid (*Ann.*, 384, 233).
**p*-Di-orsellinic acid (lecanoric acid) (*Ber.*, 46, 1143 (1913)).
o-Di-orsellinic acid (*Berl., Akad.*, 1913, 507).
m-Digallic acid (*Ber.*, 46, 1124 (1913)).
Di-syringic acid †.
Di-*o*-cumaric acid (*Ann.*, 391, 363).
Di-ferulic acid (*Ann.*, 391, 362).
Di-β-hydroxy naphtholic acid (*Ann.*, 391, 356).
p-Hydroxybenzoyl-*m*-hydroxybenzoic acid †.
m-Hydroxybenzoyl-*p*-hydroxybenzoic acid †.
Salicylo-*p*-hydroxybenzoic acid †.
Vanilloyl-*p*-hydroxybenzoic acid (*Ann.*, 372, 51).
Feruloyl-*p*-hydroxybenzoic acid (*Ann.*, 391, 360).
α-Hydroxy naphthoyl-*p*-hydroxybenzoic acid (*Ann.* 391, 354).
Orsellinoyl-*p*-hydroxybenzoic acid (*Ber.*, 46, 1141 (1913)).
Protocatechuyl-*p*-hydroxybenzoic acid (*Ber.*, 42, 1484 (1909)).
Galloyl-*p*-hydroxybenzoic acid (*Ber.*, 41, 2888 (1908)).
Pyrogallol carboyl-*p*-hydroxybenzoic acid (*Ber.*, 46, 2396 (1913)).
Syringoyl-*p*-hydroxybenzoic acid†.
p-Hydroxybenzoyl syringic acid†.
Pentamethyl-*m*-digallic acid (*Ber.*, 45, 2718 (1912)).
Pentamethyl-*p*-digallic acid (*Ber.*, 46, 1130 (1913)).
Vanilloyl-vanillin (*Ann.*, 372, 63).

TRIDEPSIDES.

*Di-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid (*Ann.*, 372, 38).
Vanilloyl-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid (*Ann.*, 372, 55).

Digitized by Google

TETRADEPSIDES.

Tri-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid (*Ann.*, 372, 43).

Vanilloyl-*p*-hydroxybenzoyl-*p*-hydroxybenzoic acid (*Ann.*, 372, 59).

LICHEN SUBSTANCES.

The only natural sources of the depsides have, until now, been the lichens, those peculiar plant forms, which, according to the discovery of Simon Schwendener, arise through symbiosis of algae and molds. To these singular morphological properties correspond also their peculiar position in chemical respects, and particularly, their content of depsides. Among the latter, the best known is lecanoric acid, which has long been regarded as an ester-like anhydride of orsellinic acid, without anything certain having been found out about the position of the depside group.

Very closely related is evernic acid, which can be regarded, on account of it splitting by bases, as an ester-like anhydride of orsellinic acid and everninic acid. The synthetic investigations which I, in conjunction with my son, Hermann O. L. Fischer,[66] have so far carried out, have been limited to these two acids.

The synthesis of lecanoric acid is carried out in the following manner: After the preparation of the crystalline dicarbomethoxyorsellinoyl chloride had succeeded, this was coupled with orsellinic acid in aqueous alkaline acetone solution at —15° and the resulting dicarbomethoxy compound saponified by a two-hour treatment with excess *N* sodium hydroxide at 20°. Thereby a diorsellinic acid results in good yield and this has proven identical in every respect with a sample of the natural lecanoric acid, which we owe to the kindness of Mr. O. Hesse in Feuerbach.

The final proof of identity rests on a comparison of the change of the natural and the artificial preparations into the methyl ester of trimethyllecanoric acid by diazomethane. This ester possesses a sharp melting point, which was the same for both preparations and also for their mixture.

Simultaneously with these investigations, my former co-worker, K. Hoesch[67] has derived orsellinic acid itself from orcyl aldehyde, prepared by the Gattermann synthesis, in which he oxidized the

[66] *Ber.*, 46, 1138 (1913); further, *Sitzungsber. d. Berliner Akademie*, 1913, p. 507.

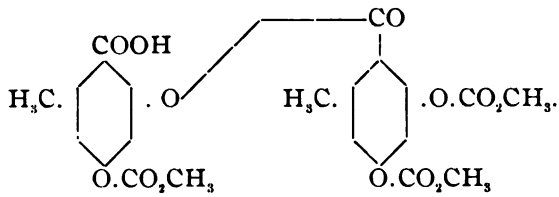
[67] *Ber.*, 46, 886 (1913).

Digitized by Google

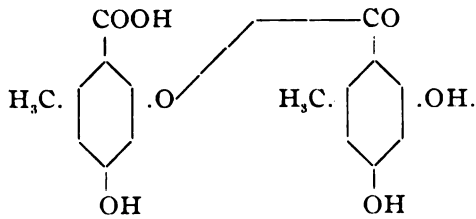
carbomethoxy compound of the latter with permanganate, and then split off the carbomethoxy groups, just as Freudenberg and I[68] recommended for the change from vanillin into vanillic acid.

Besides the synthesis, we could also supply the proof that the depside union was in the *p*-position. This was already probable by the very strong red-violet coloration of the dicarbomethoxy lecanoric acid with ferric chloride. Still more conclusive is the preparation of *o*-diorsellinic acid and its difference from lecanoric acid.

For this second synthesis, we first attempted to couple dicarbomethoxyorsellinoyl chloride with the monocarbomethoxyorsellinic acid, which contained the free phenol group in the *o*-position, in alkaline acetone solution. The failure of the experiment caused us to choose the previously mentioned indirect way from monocarbomethoxyorcyl aldehyde. This can be coupled without difficulty in alkaline acetone solution, with dicarbomethoxyorsellinoyl chloride. The tricarbomethoxyorsellinoylorcyl aldehyde resulting, in good yield, can have only the following structure:



By oxidation with permanganate, it is transformed into the tricarbomethoxy *o*-di-orsellinic acid, from which there results, on saponification with dilute ammonia, with very good yield the *o*-di-orsellinic acid.



This differs from lecanoric acid in many properties; in particular by the coloration with ferric chloride, with which it shows

[68] *Ann.*, **372**, 68 (1910).

Digitized by Google

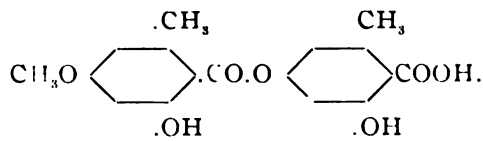
in aqueous alcohol solution not the intense purple color but rather a brown-red coloration.

We had hoped that the *o*-di-orsellinic acid would be identical with the gyrophoric acid, which likewise is found in lichens, and which, according to its splitting by alkali, has been held to be isomeric with lecanoric acid. But the comparison of the synthetic preparation with a sample of natural gyrophoric acid, which likewise Mr. O. Hesse most kindly placed at our disposal, has proven their complete dissimilarity, and from this we draw the conclusion that the gyroporic acid cannot be a didepside of orsellinic acid, but must possess some other constitution. This observation shows how very useful syntheses are in deciding important structural questions in the chapter of the lichen substances.

As an other example of this I can cite the structure of evernic acid, which my son and I have cleared up in the following way: The acid, a sample of which we obtained again from Mr. Hesse was, similarly to lecanoric acid, dissolved by an ethereal solution of diazomethane on long standing and shaking and transformed into a beautifully crystalline neutral ester, which we have identified by melting point, mixed melting point, solubility and analysis, with the methyl ester of trimethyllecanoric acid.[69]

Thus evernic acid must be a monomethyllecanoric acid, and since the everninic acid resulting from its hydrolysis is a *p*-methyllecanoric acid,[70] in evernic acid the methyl group must be in the *p*-position to the depside group.

Therefore, this gives, as the only possibility for evernic acid, the following structural formula:



I hope that now the synthesis of evernic acid can also be carried out from everninic acid and orsellinic acid according to the method of synthesis of lecanoric acid.

[69] The investigation will be published shortly.

[70] E. Fischer and K. Hoesch, *Ann.*, 391, 35 (1912).

Digitized by Google

TANNING SUBSTANCES.

Under this name are now collected together a large number of plant substances which possess the common property of combining with animal hides. They fall in wholly different groups as soon as one employs a chemical view-point for their classification. Our investigations are limited to the tanning substance of the nutgalls, the so-called tannin, and a few substances belonging to the same type. I can describe them in short as acyl-like compounds of sugar with phenolcarbonic acids.

The history of the tannins, which dates back into the 18th century is so extensive, that I, therefore, must desist from giving it completely here. Thus, I will be content by giving again, with slight amplification what is quoted in the first paper by Freudenberg and myself "On Tannin and the Synthesis of Similar Substances."

Adolf Strecker,[71] on the basis of extended investigations, came to the conclusion that tannin was a compound of glucose and gallic acid, for which he derived the formula $C_{7}H_{22}O_{17}$. That would correspond to a combination of 3 mols of gallic acid and one mol of glucose. When he later succeeded,[72] first by silver nitrate or arsenic acid and then also by phosphorus oxychloride,[73] in obtaining a glue-precipitating substance from gallic acid, H. Schiff[73] declared this to be the essential constituent of tannin, gave for it the formula $C_{14}H_{10}O_{9}$ and named it digallic acid. This formula had been recommended long before by Mulder but was contested by Strecker. The result of Strecker in regard to the formation of glucose from tannin was later substantiated by several investigators; for example Ph. van Tieghem[74] and H. Pottevin,[75] who effected the hydrolysis with the enzyme of *Aspergillus niger*. The results fluctuated noticeably in regard to the quantity of sugar. Further,

[71] *Ann.*, **81**, 248 (1852); **90**, 328 (1854).

[72] J. Löwe, *J.*, **1867**, 446; **1868**, 559.

[73] H. Schiff, *Ber.*, **4**, 232, 967 (1871); *Ann.*, **170**, 43 (1873); *Ber.*, **12**, 33 (1879); *Chem. Ztg.*, **19**, 1680; cf. also the citation on p. 1172; further, the contradictory statements of Freda (*Gazz. chim. ital.*, **8**, 9 and 363 (1878) and **9**, 327 (1879)) and Bignelli, *Chem. Zentr.*, **1909**, II, 1861, 1863; **1910**, II. 23; *Gazz. chim. ital.*, **39**, II (1909); *Rend. Soc. Chim. Ital.*, **11**, (1911).

[74] *Annal. d. Sciences naturelles V. Serie Botanique*, **1867**, 210.

[75] *Compt. rend.*, **132**, 704 (1901).

Digitized by Google

since, on the other hand, the formation of sugar has been wholly disputed, the view of Schiff has so well maintained itself, that tannin has been represented in the text-books until recently rather generally as digallic acid. In opposition to this, stands its optical activity, which was observed by Ph. van Tieghem, C. Scheibler, Flavitzky and Gunther,[76] and was used by the last as an argument against the formula of Schiff. Experiments are not lacking to remove this theoretical difficulty,[77] but the determination of the molecular weights and the careful observations of P. Walden[78] on the electrical conductivity, the light absorption and the behavior towards arsenic acid, has undoubtedly shown that tannin and Schiff's digallic acid are different. The difference became still greater when I succeeded in obtaining digallic acid in a crystalline condition and establishing its composition with certainty.[79] Meanwhile, M. Nierenstein, from numerous investigations had reached the conclusion that tannin is essentially a mixture of digallic acid and optically active leucotannin. This view cannot stand criticism. It is in opposition to the older observations on molecular weight and acidity of tannin, and our further investigations[80] have not given the slightest support for the correctness of Nierenstein's conclusions. The same judgment holds for the assertions of R. J. Manning, who claimed to have isolated from tannin a pentaethyl ester of pentagalloyl glucoside, for the preparation described by him is none other than ethyl gallate.[81] In opposition to Nierenstein, K. Feist[82] arrived at the view that tannin was really a compound of glucose and he has expressed the feeling that tannin from Turkish nutgalls is a combination of glucogallic acid with two ester-like bound molecules of gallic acid. As foundation for this view, he used his

[76] Cf. historical by E. v. Lippmann, *Ber.*, **42**, 4678 (1909).

[77] Cf. Dekker, *Ber.*, **39**, 2497 (1906) and Nierenstein, *Ibid.*, **41**, 77 (1908); **42**, 1122 (1909); **43**, 628 (1910).

[78] *Ber.*, **30**, 3151 (1897); **31**, 3167 (1898). His observations were substantiated and supplemented by Manea (*Diss., Geneva*, 1904).

[79] *Ber.*, **41**, 2890 (1908); further, E. Fischer and K. Freudenberg, *Ibid.*, **46**, 1124 (1913).

[80] E. Fischer, *Ber.*, **41**, 2890 (1908); further, E. Fischer and K. Freudenberg, *Ann.*, **384**, 225 (1911).

[81] Cf. H. C. Biddle and W. B. Kelley, THIS JOURNAL, **34**, 918 (1912).

[82] *Ber.*, **45**, 1493 (1912); further, *Chem. Zentr.*, **1908**, II, 1352.

Digitized by Google

observation that a crystalline compound of gallic acid and glucose could be isolated from Turkish nutgalls, which he regarded as an α-glucoside of gallic acid or its anhydride.[83]

In the first place, we have accorded to the results of Feist a greater weight,[84] than he really deserves. His complete publication[83] shows that noticeable inconsistencies exist in the analyses, and, above all, shows that the synthetic β-glucoside of gallic acid[85] prepared by H. Strauss and myself differs so greatly from the preparation of Feist that I can no longer regard the latter as a simple glucoside of gallic acid. What Feist in reality had in hand is not yet clear to me.

Of much more importance have proven the statements of Herzig and his students on the origin and splitting of methylotannin and I will later come back to this more fully.

Our first investigation was concerned with the fundamental question whether the glucose found by Strecker and his followers was really a constituent or only a chance impurity of tannin. For this, above all, the purest possible preparation was necessary. Since the earlier known process for the purification of tannin seemed faulty to us, we have worked out a special method. It consists in extracting the aqueous solution of the best technical tannin, saturated with a slight excess of alkali, with ethyl acetate.[86] In the description of the process we were anticipated by Paniker and Stiasny,[87] who discovered it independently. As a particular advantage of the same, we regard the condition that, by it, all real acids or, as we believe, all substances with a free carboxyl are removed. This conclusion is also important for judgment of the structure of tannin, for it appears to me that it contains no free carboxyl and, therefore, cannot be a derivative of a glucosidogallic acid. We have applied the purification process to different kinds of commercial tannin and thereby obtained preparations which we could regard as essentially identical. In addition, I will here emphasize the fact that we have used only the tannin thus purified for all the determining experiments and,

[83] *Arch. Pharm.*, **250**, 668 (1912).
[84] Fischer and Freudenberg, *Ber.*, **45**, 2713 (1912).
[85] Fischer and Strauss, *Ibid.*, **45**, 3773 (1912).
[86] Fischer and Freudenberg, *Ibid.*, **45**, 919 (1912).
[87] *J. Chem. Soc.*, **99**, 1819 (1911).

Digitized by Google

indeed, a preparation that proved identical with a product prepared from Chinese nutgalls (Zacken-gallen), and for which the specific rotation in 1 per cent. aqueous solution was + 70° to 75°. That this preparation was entirely homogeneous one cannot state with more certainty, since an essential property of homogeneous bodies, the crystalline habit, has so far not been observed for it. On the other hand, the absence of this property cannot be regarded as a proof for a high degree of impurity, since with such high molecular substances as tannin the crystalline condition is to be regarded as a more than lucky chance.

With the purified preparation we first repeated the investigation of Strecker on the hydrolysis with sulphuric acid; whereby it has become evident that, for the completion of the action with 5 per cent. acid, about 70 hours' heating at 100° is necessary, while by use of 11 per cent. acid, as Strecker employed 24 hours suffices. We believe that this slow course of the hydrolysis often has hindered the finding of sugar in the control of Strecker's investigation. To this is due the relatively small quantity of sugar noted, which we found as a rule to be between 7 and 8 per cent., while Strecker observed 15 to 22 per cent. That the higher figures of Strecker were due to his different raw material—at that time tannin was prepared preferably from Turkish nutgalls—is highly probable, but can only be decided by new investigations. Besides, we have purified tannin according to other methods, for example through the potassium salt, and on subsequent determination of the sugar reached the same results. Since, finally, control experiments with mixtures of gallic acid and glucose made clear the error of the method employed, there remains no longer any reason to doubt the results of hydrolysis also in the quantitative respect. They led to the conclusion that in the purest tannin investigated by us one mol of glucose is combined with about 10 mols of gallic acid. Naturally the thought occurred to us to isolate intermediate products, in order, from their composition, to secure further data for judging the structure. But these investigations have been completely fruitless, due to the unpleasant properties of these substances which exclude every guarantee of their homogeneity.

Besides gallic acid, no other phenolcarbonic acid has so far

Digitized by Google

been found in tannin, and our own investigations in this respect have given nothing new. The same holds for the hydrolysis with excess alkali, which begins at ordinary temperatures and on exclusion of air yields large quantities of alkali salt of gallic acid in relatively pure condition. Also here it appears to be very difficult to isolate homogeneous intermediate products. Under these conditions, it appeared desirable to proceed in the synthetic way in order to obtain an insight into the structure of the tannins. We have proceeded from the conception, that tannin contains no carboxyl and that thus all the gallic acid must be bound as an ester. This condition will be fulfilled if we can regard tannin as an ester-like combination of one mol glucose with five mols digallic acid according to the manner of pentacetyl glucose. Bold as the hypothesis may appear at first glance, it has become the center point of all further investigation and through it has gained in probability. However, we must first choose a more modest goal for the synthesis, the pentagalloyl glucose, as the digallic acid is too difficultly accessible and also because its complicated composition introduces particular difficulty on the experimental side.

PENTAGALLOYL GLUCOSE.

For the complete acylation of glucose, there have been found until now three methods: (1) Boiling with acid anhydride in presence of sodium acetate or zinc chloride. The best known example is the preparation of pentacetyl glucose, from which results, according to the catalizer used, the α- and β-form. (2) Treatment with acid anhydride in presence of pyridine (Behrend). According to whether one starts with α- orβ-glucose, there results the α- or β-form. (3) Treatment with acid chloride in aqueous alkali solution (E. Baumann). The process has only been completely studied for benzoyl chloride, and gives only one pentabenzoyl glucose of m. p. 186–8°. For gallic acid, none of these processes was applicable, and even for the chloride of tricarbomethoxygallic acid the application was excluded in aqueous alkaline solution, because there would inevitably follow the destruction of the carbomethoxy groups. We were thus forced to search for a new process and have found it in the combined action of the chloride with tertiary bases, for which quinoline has proven to

Digitized by Google

serve particularly well. As a solvent we used dry chloroform, the chloride being very easily taken up in this. However, the glucose is especially difficultly soluble in it. But if it was shaken in finely pulverized condition with chloroform, quinoline and a moderate excess of tricarbomethoxygalloyl chloride for 24 hours, complete solution ensued. By precipitation with methyl alcohol, the product of this coupling may be easily isolated. After appropriate purification, there is formed a feathery, colorless, amorphous powder. We have designated it as pentatricarbomethoxygalloyl glucose. By careful saponification with excess of alkali in aqueous acetone solution at the ordinary temperature, there was obtained from this a tannin which we regarded as pentagalloyl glucose and which now shows surprisingly close similarity to tannin. An essential difference was evident only in optical rotation and the quantity of gallic acid which resulted on hydrolysis with sulphuric acid.

However, I will not be reticent on the difficulty which the establishment of the empirical composition of such amorphous products involves, especially since the percentages for carbon and hydrogen differ only very slightly between pentagalloyl and tetragalloyl glucose. But we have convinced ourselves in simpler cases, for example, in derivatives of benzoic, hydroxybenzoic and salicylic acids, where the analytical differences for penta- and tetraacyl bodies are very much greater, that the process in fact gives the pentaacyl compound, and thus there exists no important ground for assuming that with galloyl bodies the reaction follows another course.

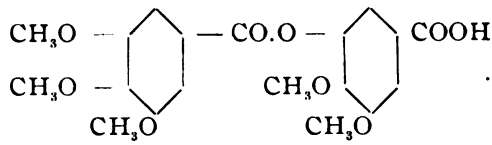
In spite of all this, the homogeneity of pentagalloyl glucose is very doubtful; we hold it rather to be a mixture of two stereoisomers, for the investigation to be cited later, on the benzoylation of glucose in the same way, has shown that different products result, which owe their origin to the α- or β-glucose. Here the pure α- or β-benzoyl glucose can be isolated by crystallization, but the yield and other considerations show that in the crude product there exists a mixture of the two forms. The same could well hold in the case of the galloyl bodies, only here the separation of the pure substances is not possible on account of their amorphous nature.

Digitized by Google

The pentagalloyl glucose is closely related to tannin in all its properties, so that with its artificial preparation the principal aim of the synthesis seems to be attained. But before one can speak of a complete solution of the tannin question its synthesis also must be realized. How far we have approached to this goal, the investigation on the synthesis of tannin and methylotannin will show.

Methylotannin results, according to the researches of Herzig[88] and his students, from the action of diazomethane on tannin. Since it is wholly indifferent towards alkali, one must assume that it contains neither carboxyl nor free hydroxyl groups. On hydrolysis, it yields according to Herzig, trimethylgallic acid and the unsymmetrical *m,p*-dimethylgallic acid. Combining these observations with the previously advanced conception of the constitution of tannin, the conclusion follows that tannin is essentially an ester-like compound of glucose with five mols *m*-digallic acid, and the corresponding methylotannin the combination of glucose with five mols pentamethyl *m*-digallic acid.

The following investigation on the synthesis of methylotannin rests on these considerations, and demanded large quantities of the hitherto unknown pentamethyl *m*-digallic acid:



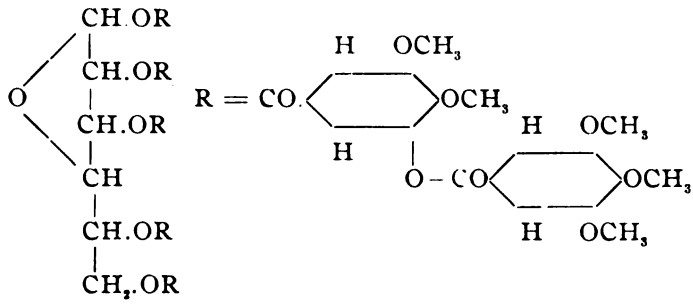
This was prepared from trimethylgalloyl chloride and *m,p*-dimethyl ether gallic acid, and for the latter we discovered a new, rather good method of preparation,[89] by coupling in an aqueous alkaline solution.[90] In the same manner the isomeric pentamethyl-*p*-digallic acid[91] resulted from trimethylgalloyl chloride and syringic acid. For differentiating the two isomers, the methyl esters, which have been recently described by Mauthner,[92] serve very well, since they possess sharp melting points.

The pentamethyl-*m*-digallic acid yields, further, a beautifully

[88] *Ber.*, **38**, 989 (1905); *Monatsh.*, **30**, 543 (1909).
[89] Fischer and Freudenberg, *Ber.*, **45**, 2717 (1912).
[90] *Ibid.*, **45**, 2718 (1912).
[91] *Ibid.*, **46**, 1130 (1913).
[92] *J. prakt. Chem.*, [2] **85**, 310 (1912).

Digitized by Google

crystalline chloride, and we have coupled this with α- as well as β-glucose, according to the method mentioned before. In both cases products resulted which are to be regarded as penta-acyl derivatives of glucose or, more exactly, as penta- (penta-methyl-*m*-digalloyl)-glucose.



They differ between themselves in optical rotation. Both are dextrorotatory in acetylene tetrachloride and benzene, but the preparation from α-glucose shows a noticeably higher rotation. By repeated resolution the optical rotation changes, and we, therefore of necessity come to the conclusion that both preparations are mixtures, most probably of two stereoisomers, *i. e.*, are derivatives of α- or β-glucose. We have now compared the preparations with a methylotannin, that we prepared from carefully purified tannin from Chinese nutgalls (Zacken-gallen) according to Herzig's directions, and have shown their great similarity, particularly with the preparation from β-glucose, the optical rotation in acetylene tetrachloride is very nearly the same.

We can scarcely doubt from these observations that the two synthetic penta-(pentamethyl-*m*-digalloyl)-glucoses are very closely related to methylotannin and probably possess the same or very similar structures. But no answer can yet be given as to a final identification; for with these high molecular amorphous bodies the general comparison methods of organic chemistry fail, and we must here, as yet, content ourselves with probabilities. Furthermore, I will not be reticent as to the fact that we have tried also to build up tannin itself artificially from *m*-digallic acid. To this end, we have first worked out the previously mentioned reliable and satisfactory method for obtaining the acid itself.

We have further proven its structure by complete methylation

Digitized by Google

with diazo methane, *i. e.*, by changing it into the methyl ester of pentamethyl-*m*-digallic acid.[93] We must make here the surprising statement that the first crystallized digallic acid, which according to the synthesis from tricarbomethoxygalloyl chloride and 3,5-dicarbomethoxygallic acid appeared to be the *p*-compound,[94] has not this structure, but probably consists chiefly of *m*-digallic acid.[95] For, complete methylation yields every time the methyl ester of pentamethyl-*m*-digallic acid, m. p. 128°. The results show again how important complete methylation is for comparison of complicated depsides.

We have tried, further, to change *m*-digallic acid into its pentacarbomethoxy compound. The reaction appeared to succeed with chlorocarbonic methyl ester and dimethyl aniline, and later the acid was isolated from the crude product by careful treatment with alkali bicarbonate. But now the difficulties began. We have in no way succeeded in obtaining the carbomethoxy compound crystalline, and the chloride derived from it also remained amorphous. Therefore, the finally attempted coupling with sugar was so unsuccessful that we cannot speak of any exact results. The synthesis of tannin in the meaning intended by us, which I hoped to be able to announce to you to-day, is thus as yet an unsolved problem.

Also the question of structure is not thoroughly answered. One can only say that our hypothesis is as yet the best expression for the observations. But it must not be forgotten that the results of elementary analysis, or of hydrolysis, give no certain differentiation between a compound of glucose with 9, 10 or 11 mols gallic acid, respectively.

To this is also added the uncertainty whether tannin, after the best purification, is homogeneous. It could just as well be a mixture of very similar substances, for example a penta-(digalloyl)-glucose with a tetra-(digalloyl)-glucose or tri-(digalloyl)-di-(galloyl)-glucose, etc.

Further, it is possible, if not also probable, that the tanning substance contains in place of glucose one of its polysaccharides.

[93] E. Fischer and K. Freudenberg, *Ber.*, **46**, 1127 (1913).
[94] *Ibid.*, **41**, 2890 (1908); *Ann.*, **384**, 225, (1911).
[95] *Ber.*, **46**, 1118 (1913).

Digitized by Google

Finally I must, in order to obviate misunderstanding, again emphasize the fact, that our observations have been limited to the tannin from Chinese nutgalls (Zacken gallen), which to-day seems to be the chief constituent of commercial tannin. It is thus not excluded that other relationships of sugar and gallic acid will be encountered, with tannins of other origin, for example, that from Turkish nutgalls.

In fact, according to the latest experiments of Dr. Freudenberg, a tannin from the so-called Aleppo-gallen (Merck), purified by the above process, shows noticeable differences. It is slightly levorotatory in aqueous solution and gave, on hydrolysis, more than 10 per cent. glucose.

But all these questions are of inferior signification, in comparison with the proof that the synthetic pentagalloyl glucose is a tanning substance of the tanning class.

OTHER NATURAL TANNING SUBSTANCES OF THE TANNIN CLASS.

There are numerous examples of sugar-containing tanning substances. But in the majority of cases treated, they are amorphous, slightly investigated products; many of them appear to be true glucosides,[96] particularly those which yield on hydrolysis aromatic phenol ketones. On the other hand, those which contain phenolcarbonic acids as constituents, appear not to be glucosides but, like tannin, to be ester-like derivatives of sugar. To this class belong, first of all, two crystalline tanning substances, the chebulinic acid of myrobalans and the Hamamelis-tannin crystallized by Gruttner in Böhm's laboratory, with which we have carried out some experiments. The first, which according to H. Thoms is identical with the "eutannin" recently introduced in the trade, yields, under exactly the same conditions as tannin, by hydrolysis with sulphuric acid, glucose which we have proven with all certainty.[97] However, the quantity of gallic acid is noticeably small. Apparently the tanning material is an incompletely acylated compound of glucose, or one of its polysaccharides, and gallic acid. Recently, the investigations of H. Thoms

[96] The earlier custom of calling all natural derivatives of glucose, which are not simple carbohydrates, glucosides, cannot be retained. I regard as glucosides only those substances which are similarly constituted to the methyl or phenyl glucosides.

[97] E. Fischer and Freudenberg, *Ber.*, 45, 918 (1912).

Digitized by Google

and his student, W. Richter, on eutannin,[98] have appeared, and contain many valuable observations, but leave the sugar content of the tanning substance doubtful. On the other hand, I must say that I cannot assent to the speculations thus founded. The chebulinic acid demands a new, complete, investigation before one can pronounce a final judgment on its structure.

The Hamamelis-tannin also gives, on hydrolysis with sulphuric acid, a sugar which is entirely different from glucose, and appears to be a hitherto unknown body.[99]

These observations show that the tanning substances can also be a source for new members of the sugar series. Dr. Freudenberg will exhaustively investigate the sugar of Hamamelis-tannin.

Whether the crystalline tanning substance of tea described by A. W. Naninga[100] also belongs here, is still to be proven.

GENERALIZATION OF THE TANNING MATERIAL SYNTHESIS.

The process which served for the building up of pentagalloyl glucose is easily applicable to other phenolcarbonic acids. As has been mentioned before, the penta-*p*-hydroxybenzoyl-glucose[101] was so obtained. It is very difficultly soluble in water and its elementary analysis undoubtedly shows it to be a penta-acyl compound. The pentasalicyloglucose which will be fully described in a later publication, possesses entirely similar properties. Just as difficultly soluble in water is the corresponding derivative of caffeic acid, which I had Mr. R. Oetker[102] prepare. The compound of pyrogallolcarbonic acid, which we have designated as pentapyrogallol carboylglucose,[103] has proven particularly interesting. It is isomeric with pentagalloyl glucose and shows in general the same behavior, although it shows a noticeable difference in its solubility in water. While the galloyl compound is easily taken up in cold water, the isomeric substance is very difficultly soluble in hot water and is practically insoluble in cold water. The same also holds for its dark colored iron compound.

[98] Work of the *Pharmazeut. Institut d. Univ. Berlin*, 9, 78, 85 (1912).

[99] E. Fischer and K. Freudenberg, *Ber.*, 45, 2712 (1912).

[100] *Mededeelingen uit's Lands Plantentuin Nr.*, 46; *Onderzoekingen betreffende d Bestanddeelen van het Theeblad.*

[101] E. Fischer and K. Freudenberg, *Ber.*, 45, 933 (1912).

[102] Will be published shortly.

[103] E. Fischer and M. Rapaport, *Ber.*, 46, 2397 (1913).

Digitized by Google

On first glance, this difference in substances of so similar a structure as the two tanning materials, appears very surprising. But it loses in significance when one remembers that tannin and also the similar pentagalloyl glucose are inclined to form colloidal aqueous solutions. This property is present only to a slight degree or not at all in the isomeric compound. Such observations merit attention for the study of colloidal solutions, for they show how dependent their formation is on small differences in the structure of the materials. On the other hand, the formation of hydrosols is of highest importance for the role which such substances play in the living world, and this applies also to their chemical characteristics, as proven by the case of the pentagalloyl glucose; for here it was not easy, on account of the difficulty in preparing aqueous solutions, to verify the astringent taste and the precipitation by glue solution.

For all the above-mentioned glucose derivatives, the same thing holds, as I have before drawn attention to in connection with the homogeneity of pentagalloyl glucose, *i. e.*, they are probably mixtures of the two stereoisomeric derivatives of α- and β-glucose.

Like the sugars, the phenolcarbonic acids can be coupled with the true glucosides, as the preparation of the tetragalloyl α-methylglucoside has proved.[104] That this also shows the characteristic properties, for example, the taste and the precipitation phenomena of tanning substances, is not surprising, since it is well known that ethyl gallate shows noticeable precipitability by glue solution. With the methyl glucoside derivatives there is obviously missing the complication which arises, as in the glucose derivatives, from the simultaneous formation of α- and β-forms.

According to the behavior of methylglucoside, it cannot be doubted that the simple polyhydric alcohols will serve for the same synthesis. We have so far combined only glycerol[105] with gallic acid, submitting the product merely to a hasty investigation, since such bodies exhibit no particular interest.

BENZOYLATION AND CINNAMOYLATION OF SUGARS AND POLYHYDROXYLATED ALCOHOLS.

By the application of the new acylation method to the simple

[104] Fischer and Freudenberg, *Ibid.*, 45, 934 (1912).

[105] Fischer and Freudenberg, *Ber.*, 45, 935 (1912).

Digitized by Google

aromatic chlorides, some new and noteworthy results were obtained. The benzoylation of glucose has been carried out formerly only in aqueous alkaline solution, giving as a final product a pentabenzoyl glucose which melted at 186–8°, and for which I, in conjunction with B. Helferich, found in chloroform solution $[\alpha]_D^{20} = 25.4°$[106] But the yield of this high melting preparation was very unsatisfactory (about 15 per cent. of the theory). A preparation of about the same rotation and similar melting point can be obtained with a much better yield, according to the new process, by shaking β-glucose with a mixture of benzoyl chloride, quinoline and chloroform. On the other hand, α-glucose gave, under the same conditions, an isomeric pentabenzoate with a much higher rotation, $[\alpha]_D^{20} = 107.6°$, whose melting point, however, was rather inconstant.[107]

That steric rearrangement takes place from the α- to the β-form or conversely, was quite probable according to the resulting yield, and was proven by the following experiment: A mixture of α-glucose, benzoyl chloride, quinoline and chloroform, in the proportions used earlier, remained standing 20 days after complete solution had taken place. There had then separated a rather large quantity of crystalline β-pentabenzoyl glucose.

Still easier than the benzoylation, is the cinnamoylation of sugar with cinnamic acid chloride and quinoline. I have prepared with Mr. R. Oetker, in this way, the pentacinnamoyl derivatives of α- and β-glucose, galactose, mannose, and the hexacinnamoyl mannite. They are all beautifully crystalline substances. By this process, the pentabenzoyl and pentacetyl mannose (m. p. 114–6°; $[\alpha]_D^{20} = -24.8°$) were obtained crystalline. The detailed description of this investigation will soon follow.

EXPERIMENTS ON THE PARTIAL ACYLATION OF SUGAR AND POLYHYDROXYLATED ALCOHOLS.

All the previously mentioned acylation experiments were directed towards the preparation of the end product and thus were carried out with an excess of acid chloride. To conduct the reaction only to an intermediate stage, the experimental conditions are also unfavorable; for the sugar on shaking goes gradually

[106] *Ann.*, **383**, 88 (1911).
[107] *Ber.*, **45**, 2725 (1912).

Digitized by Google

into solution in the acylating liquid and is thus at the beginning in contact with an excess of the chloride.

In other methods of acylation, for example, by acetylation with acetic anhydride or benzoylation according to Baumann, it is just as difficult to isolate partially acylated sugars in pure condition. One must, therefore, seek for a new method for the preparation of such products, and here reflection suggests the partial protection of the hydroxyls of the sugar by other groups which afterwards can be easily split off again. The acetone derivatives of the sugars and polyhydric alcohols, which were discovered by me, appear to be particularly useful for this purpose. Some years ago, I carried out such experiments with acetone-glycerol,[108] in order to prepare a monobenzoyl derivative with benzoyl chloride in alkaline solution. Unfortunately, the results were negative; for, under the conditions chosen, the acetone residue was split off and tribenzoyl glycerol formed. Perhaps this splitting can be avoided by excluding water according to the new acylation method, and I am already occupied in this direction. If, in such a way, the partial coupling of sugars with phenolcarbonic acids can be realized, just as Irwin has recently succeeded in the partial methylation of glucose, it will mark an important advance in the synthesis of tanning substances. For, as I have mentioned before, chebulinic acid probably belongs in this class of partially acylated sugars, and it is to be hoped that the same is the case with many other natural products which are easily soluble in water, and thus differ from the completely acylated glucose derivatives, which are as a rule difficultly soluble.

PHYSIOLOGICAL AND PRACTICAL SIGNIFICANCE OF THE SYNTHESIS OF TANNINS.

The knowledge that ester-like compounds of sugar and phenolcarbonic acids form a great class of tannin-like tanning substances, is doubtless of importance to the plant physiologists. Especially interesting appears to me the fact that the sugar of plants can be used for esterification just as well as glycerol or the monohydric alcohols. The organism tolerates free acid, in general, only at definite places, as in the maw of animals or in unripe fruits, or in bark and shells, where they probably act as defensive

[108] *Ber.*, **28**, 1170 (1895).

Digitized by Google

agents. Generally it endeavors to neutralize the acid group. This happens often by salt formation, but much oftener by amide formation, as in the proteins, or by ester formation, as in the fats. Under this now comes the esterification of sugars. Since sugars are much more widely distributed than glycerol, I do not doubt that such ester derivatives will be met still oftener in the plant kingdom and perhaps in the animal kingdom also.

I have in mind not alone the phenolcarbonic acids, but more especially the numerous hydroxy acids of plants. That one has so far overlooked their sugar derivatives, does not surprise me, since they are probably easily soluble and easily saponified bodies. It has long been my wish to prepare such combinations synthetically, but the method for this must first be found. Probably the carbomethoxy derivatives recently discovered by me and my son will play a part in it.[109] Previously I had to be contented with directing the interest of plant physiologists to these things. Perhaps we will find such esters in sweet fruits, which, in the unripe condition, contain noticeable quantities of glycollic acid and its homologs. I have myself carried out some experiments on this point, but so far without decisive results. I hope, later, to be able to communicate more definitely on this as well as on the unequal distribution of acids in the shell and meat of certain fruits, for example, the early plums.

Both the naturalist and the synthetic chemist are often confronted by the question as what practical purpose the results of his work can serve, and to myself in a circle of scholars, as I exhibited the artificial tannin and an ink prepared from it, which aside from the water was entirely synthetically derived, the question was put: Is it cheaper than the ordinary ink? The answer was naturally negative, and so it must be also for the synthetic tanning substance, so far as concerns its use in the tannery; for here only very cheap substitutes, such as the recently introduced neradol of Stiasny, come into consideration.

But the matter appears otherwise when we consider that tannins in small quantities are constituents of important comestibles, such as wine, tea, coffee and numerous sweet fruits, on whose taste it

[109] *Ber.*, **46**, 2659 (1913).

Digitized by Google

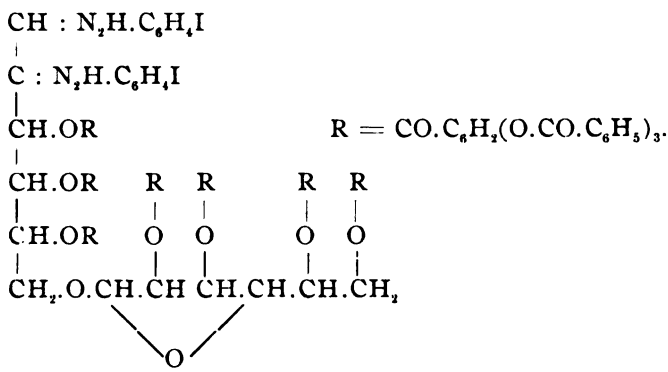
has an influence not to be underestimated. If once synthetic chemistry breaks into this important field, of which I have no doubt, then, probably the synthesis of tanning substances will be honored also in its technical applications.

HIGH MOLECULAR SUBSTANCES.[110]

Among the before-mentioned products of the tannin synthesis many substances of rather high molecular weight are found; for with the penta-(tricarbomethoxy galloyl) glucose this total amounts to 1810, and for the penta-(pentamethyl-*m*-digalloyl) glucose it rises to 2051; which has given the inducement to apply this smoothly running ester formation with the members of the sugar group to still more complicated acids. For this purpose the higher fatty acids at first appear particularly useful, such as, stearic, behenic and melissic, but finally we have found, in the derivatives of gallic acid, especially its tribenzoyl compound, a still better material; it yields a beautifully crystalline chloride, which can be completely purified and can be prepared comparatively easily in large quantity. By combination with mannite a neutral ester was prepared which has a molecular weight of 2967. The verification of the composition of such substances is rendered very difficult by the condition that the analytical differences for carbon and hydrogen are not sufficiently great to determine the number of acyl groups with certainty. On this account we have incorporated in the molecule halogenated groups, in order to have the percentage of halogen as a measure for the molecular weight of the final product. For this purpose, we have used the *p*-iodophenyl maltosazone, which on the one hand is distinguished by its fine crystalline state, and on the other hand by a high content of halogen (33 per cent.). Its coupling with tribenzoyl-galloyl chloride yielded hepta-(tribenzoylgalloyl-*p*-iodophenyl maltosazone, which, though amorphous, still possesses very fine properties, and on analysis gave such sharp figures that we have no hesitation in proclaiming it as a chemical individual. Its structure follows from the synthesis and corresponds to the following formula, in which R denotes the tribenzoyl gallic acid:

[110] E. Fischer and K. Freudenberg, *Ber.*, 46, 1116 (1913).

Digitized by Google



Hepta-(tribenzoyl galloyl)-*p*-iodophenyl-maltosazone, $C_{220}H_{142}O_{58}N_4I_2$.
(Molecular weight 4021.)

The only uncertainty in the formula is the structure of the maltose residue, *i. e.*, the coupling of the two glucose residues, a question, which in the foregoing case has no significance. The molecular weight amounts to 4021. The substance with this molecular weight stands at the head of all organic substances of known structure derived wholly by synthesis.

We have finally proven, by freezing point determination in bromoform solution, that it, as well as a moderately closely related substance, for example, hexa-(tribenzoyl galloyl)-mannite, still satisfactorily obeys Raoult's law. The hepta-(tribenzoyl galloyl)-*p*-iodophenyl-maltosazone exceeds in molecular weight the highest product of the polypeptide synthesis, the *l*-leucyl-triglycyl-*l*-leucyl-triglycyl-*l*-leucyl-octaglycyl-glycine, by more than three times, and I believe, that it is also superior to the majority of natural proteins. However, for the beautifully crystalline oxyhemoglobin, as is well known, a molecular weight of 16,000, has been derived from its iron content, but against such calculations the objection can always be made, that the existence of crystals in no way guarantees chemical individuality, particularly since it can be regarded as an isomorphous mixture, such as the mineral kingdom so often presents to us in the silicates. Such objections vanish with synthetic products, whose formation can be controlled by analogous reactions.

The molecular physicists would do well in the study of high molecular substances to confine themselves to the synthetic prod-

Digitized by Google

ucts of known structure. I will continue the experiments on the building up of giant molecules with the aid of the processes described.

Certainly it offers in other respects a great incentive to test the productiveness of our methods. As is well known, the modern physicist is endeavoring to split up matter into smaller and smaller pieces. One is long since past the atom, and how long the electrons will be for us the smallest particles of matter, cannot be predicted. It seems to me that organic synthesis is called upon to accomplish the converse, *i. e.*, to accumulate larger and larger masses in the molecule, in order to see how far the compression of matter can go, in the meaning of our present conceptions.[111]

I hope that the results to date will give an effective stimulus in this direction.

LIGHT LEATHER LIMING CONTROL.*

Report by Joseph T. Wood.

Since the report presented to the London Conference in 1912 (*Collegium*, 1912, 557) on the Control of Liming, when the scheme published in *Collegium*, 1913, p. 73, was provisionally adopted, the following papers relating to the liming process have appeared:

1. Provisional Method of Analysis of Lime Liquors. *Coll.*, 1913, 73.
2. Il lavoro di calce. Cav. Uff. Ettore Andreis, Il Conciatore, Torino. (see also *Coll.*, 1913, 23.)
3. The Liming Problem. A. Seymour-Jones, H. R. Procter. *Coll.*, 1913, 14.
4. Depilatories and their influence upon hides, R. W. Griffith. J. A. L. C. A., 1913, 224.
5. The determination of Alkaline Sulphides, Douglas McCandlish and John Arthur Wilson, J. A L. C. A., 1913, 28, *Coll.*, 1913, 80. In German p. 127.
6. Unhairing and Liming, W. Eitner, *Der Gerber*, 1913, 225—7, 239—41, 253—5, J. A. L. C. A., 1913, 482.

[111] Cf. H. Crompton, *Proc. Chem. Soc.*, **28**, 193 (1912).

* *Collegium*, 1914, 305-11.

Digitized by Google

7. J. T. Wood, H. J. S. Sand, D. J. Law, *Coll.*, 1913, 364.
8. Neues Aescher-Verfahren, Dr. E. Giusiana, (*Le Cuir*, 1912, No. 19), *Coll.*, 1913, 515. J. A. L. C. A., 1912, 682.
9. J. R. Blockey. Graphic Method, *Coll.*, 1913, 629. J. A. L. C. A., 1913, 383.
10. Notes on Depilating, Allen Rogers. J. A. L. C. A., 1914, 42. (See also article by "Morand," L. T. R. Febr., 1914, p. 109.)
11. The Estimation of Sulphides in Lime Liquors. J. R. Blockey and P. V. Mehd, *Coll.*, 1914, 73. J. A. L. C. A., 1914, 203.

Griffith (4) considers that chemical control of limes can never be effective unless it includes the examination of the hide also. This is undoubtedly true, but such work is of necessity best done in the Works laboratory, and emphasizes the importance of histological and microscopical examination.

Andreis (2) draws attention to the beneficial effect of ammonia in the limes when kept within proper limits, and states that this is best attained by the three-pit system. He is still working on the problems connected with liming.

Seymour-Jones (3) asks the question: Is liming a necessity? In this connection Wood (The Puering and Bating of Skins, p. 139) has also stated that it is probable that a skin which has never been submitted to the liming operation could be bated by the action of enzymes alone without addition of ammonia compounds, and still make good leather. Dr. Otto Röhm has attempted to solve the problem by the introduction of an enzyme preparation whereby the skin is unhaired and bated at one operation (*Coll.*, 1913, 374. J. A. L. C. A., 1913, 408.) If this is successful in practice, the preparation of skins for tanning would be vastly simplified. Since no alkali would be introduced into the skin, all the various processes for getting rid of it would be done away with, and the preliminary operations could be conducted antiseptically.

Procter (3) remarks that primarily we lime a hide to remove the hair and epidermis structures, but produce at the same time other effects, some of which are useful, but which might be pro-

Digitized by Google

duced in other ways. Payne, in a communication to the writer, considers that the addition of calcium to the hide fiber is necessary for the proper formation of leather, at any rate, for vegetable and oil tannages.

Eitner (6) in an interesting series of articles in *Der Gerber,* distinguishes between the unhairing effect and the liming effect. Unhairing may be conducted under sterile conditions by the use of alkaline sulphides, and the bacterial effect may be produced in the bates where it can be more effectively watched.

Wood, Sand and Law (7) have given a method of expressing numerically the swelling effect of limes, and give a number of results obtained in the liming of sheep skins.

Allen Rogers (10) gives the results of a number of practical tests carried out at the suggestion of the American National Association of Tanners. Experiments were carried out to ascertain the various amounts of lime on the swelling and absorption of lime, as the idea is prevalent in some quarters that, so long as lime is present in excess, the actual amount of that excess makes no difference to the result. It was found that a larger amount of lime produces a greater increase of weight of the raw skins, and causes a greater absorption of lime by them. For instance, 5 per cent. of lime acting for two days produced 40 per cent. increase of weight, and was absorbed to the extent of 1.3 per cent. on the weight of the hides, while a 10 per cent. acting for the same time produced 50 per cent. increase of weight, and 5.6 per cent. was absorbed. It was found that in all cases where lime was applied fresh, the loss of hide substance was greater than when the lime was "bettered," new lime having a greater solvent action on hide than old. Eighty per cent. of the total increase in weight of the hide during liming was obtained during the first day in lime, and most of the lime taken up by the hide is absorbed during the first two days. Practically all the fat which is saponified becomes so during the first 24 hours. To account for the less solvent action of an old lime than of a new, the author suggests that a used lime may exercise a protective colloid effect.

From these results it is concluded that the proper practical way to apply a straight lime liquor is to enter the goods into lime a

Digitized by Google

few days old at most, and then work up through the series through a fresh liquor. "Hydrated lime," is said to be rapidly replacing slaked lump lime for tannery use, and to offer many advantages.

The method of liming, with a mixture of sodium sulphide and calcium chloride, is said to have the advantages of freedom from false grain, complete removal of hair, saving of time and better measurement. The goods are run in a 20° Bk. (S. G. 1.020) containing calcium chloride to the extent of quarter of the weight of sulphide.

Dr. E. Giusiana (8) has published a method of liming for cases where it is not desirable to swell the skin. He adds calcium chloride to sodium sulphide solution in equivalent proportions according to the formula:

$$Na_2S + 2H_2O + 2CaCl_2 = 4NaCl + Ca(OH)_2 + Ca(SH)_2$$

He also states that the addition of magnesium and ammonium salts gives a very fine grain. The composition of the "lime" per thousand liters is:

Na_2S	5 kilos
$CaCl_2$ (Cryst.)	8.7 kilos
$MgCl_2$	8.05 kilos
NH_4Cl	2.10 kilos
$BaCl_2$ (Cryst.)	9.65 kilos

The pit may be used a second time by strengthening with half the above quantities.

The writer wishes to note here that this process was communicated to him by Professor E. Stiasny in 1911 in a letter.

Blockey (9) gives curves showing graphically the amount of hide substance lost during the liming of a pack of hides, and also the amount of hide substance in a lime during the ageing of the liquor. The first shows that one per cent. of the hide is dissolved in ten days liming; the second shows that, after ten days, a lime in which hides have continually worked contains three grams of hide substance per liter.

Blockey and Mehd (11) point out that the failure of McCandlish and Wilson (5) to obtain correct results by their method is due to the fact that they omitted to add ammonium chloride in preparing the reagent, which should consist of a N/10 solu-

Digitized by Google

tion of zinc sulphate, to which has been added ammonia until the precipitate has just redissolved, and also 50 grams of ammonium chloride per liter. McCandlish and Wilson also use liquors of much lower concentration than are met with in practice. The mechanism, from the point of view of the ionic hypothesis, of the reactions involved in the estimation of sulphide in lime liquors with zinc sulphate, is discussed. When the method is carried out as described in Procter's "Leather Chemists' Pocket Book," p. 34, it is quite reliable. Nickel chloride preferred by some chemists as outside indicator.

The author wishes to call attention to some conclusions which may be drawn from the preliminary report by D. J. Law and himself (*Coll.*, 1912, p. 121). The amount of nitrogen dissolved by lime liquors increases with the age of the lime, or rather with its nitrogen content. The following table shows the amounts of N in grams per liter dissolved at each draw in a series of limes:

I = New lime.
II = The same used for a second lot of skins.
III = The same used for a third lot of skins.

The skins in I and II had already been through 2 weaker limes. The skins in III had not been in another lime, which accounts for the somewhat higher figure for N in first draw.

	I	II	III
First Draw	0.1904	0.3108	0.4438
Second Draw	0.1524	0.1736	0.0840
Third Draw	0.1120	0.1736	—
Fourth Draw	0.0728	0.0784	—
Total	0.5276	0.7364	0.5278

In each case it will be noted that the greatest amount of nitrogen is dissolved in the first draw. It would appear that there is a definite amount of nitrogenous substance which the limes are capable of extracting from the skin. The total amount of nitrogen dissolved from the three packs of skins in question does not differ widely. The limit of nitrogen which may be allowed in a lime before running it away is somewhat difficult to fix. It may be assumed that up to 0.2 gram, per liter, the nitrogen is not detrimental, but this depends upon a number of other factors:

Digitized by Google

temperature, degree of breaking down of the proteids present, and on the number of proteolytic bacteria present, so that each individual case must be judged on its merits. For analyses of old limes the paper of Wood and Trotman[1] may be referred to

Mr. R. Farraday Innes has communicated to the writer the following unpublished results obtained in the analyses of sulphide lime liquors before and after goat skins. See table below.

Days in liquor	cc. N/10 HCl per 10 cc. (Methyl red)	Grams S per liter	Grams N per liter	Remarks
0	7.5	0.29	1.29	Mellow before green goods.
8	7.2	0.16	1.94	Same after green goods.
8	6.9	0.55	0.84	New before same goods.
14	7.9	0.42	1.30	Same after goods.
0	5.7	0.24	1.03	Mellow before green goods.
6	6.9	0.19	1.70	Same after green goods.
6	5.2	0.35	0.29	New before same goods.
11	6.7	0.32	0.70	New after same goods.

No regular results or curves of absorption of lime could be obtained, and as much as 14 per cent. of CaO on a fully limed goat skin was found. In all cases the ash percentage confirmed the CaO, which was usually 65 to 75 per cent. of the ash. The figure shows graphically the absorption of lime by goat skins obtained by Innes.

The question of time in liming, as in tanning, is of great importance. Not only must the amount of lime in the skin be taken into consideration, but also the length of time during which it has acted. A skin may absorb a good deal of lime without being properly swollen. The explanation of the swelling of skin and gelatin by acids and alkalis is of great general interest. The discovery by Professor Procter (Trans., 1914, 313; and *Collegium*, 1914, p. 194. J. A. L. C. A., 1914, 182) that in the acid swelling of gelatin an ionized salt of gelatin is formed, which is the cause of the osmotic pressure produced, is of far reaching importance, not only to tanning chemists, but also to physiologists. This salt behaves in the same way as inorganic salts of diacid constitution, and consequently its properties can

[1] *J. S. C. I.*, 1909, 1304. *Coll.*, 1910, 181. *J. A. L. C. A.*, 1910, 272.

Digitized by Google

be explained by the ionic theory, and it is unnecessary to introduce any special explanation to account for the phenomena observed.

Professor Procter finds that the swelling of gelatin in dilute acid solutions depends on the osmotic pressures and equality of products of a diacid ionizable salt of gelatin as a base, and of the external acid with which it is in equilibrium; and the ionization-constants and molecular weight being known, all the other quantities are determined. The method is general and applicable to other proteins and other acids.

The ionic concentrations in the jelly are all mathematical functions of that of the equilibrium acid, and independent of the chemical nature of the gelatin or other protein.

While gelatin jelly in equilibrium with an acid is believed to be a molecular solution, jellies and colloid solutions, in which the conditions of equilibrium are not fulfilled, are probably two-phased structures, and may exhibit the pores described by Bütschli and van Bemmelen.

The case of swelling of skin by hydroxyl ions is known to be different to that produced by hydrogen ions (See Procter Colloidal Chemistry B. A. A. Rep., 1908, p. 19), but there seems no reason to doubt in the light of Professor's Procter's discovery that, in this case also, a salt of gelatin or collagen, is formed, which is almost as completely ionized as a solution of caustic soda. In this case the gelatin must function as an acid, and form a "gelatinate" of calcium.

The author has observed a very remarkable change in the case of sheep skins which have been over-limed. In the early stages of liming the hyaline layer is not attacked by tryptic enzymes, even by long exposure to their action, but after a certain time in lime, these enzymes are capable of attacking this layer. The observation has been confirmed by Dr. Otto Röhm, of Darmstadt, but its explanation necessitates a research into the chemical nature of the hyaline layer, which it is hoped will shortly be undertaken.

Professor Stiasny has made some experiments to judge the constitution of an old lime by physical measurements. He found that peptones diminish considerably the surface tension, but do

Digitized by Google

not increase the viscosity directly. Inorganic substances (lime, sulphide) have practically no influence on either surface tension or viscosity. It is not impossible that the figures obtained for these quantities will give valuable information in addition to that obtained by chemical methods.

Starting from the idea that the effect of different components of an old lime on the surface tension, and on the viscosity might prove of sufficient difference to allow some conclusions to be drawn from these two figures, it was found that simple (crystalline) inorganic compounds like lime and sodium sulphide, have practically no effect on σ (surface tension) and η (viscosity).

Further that glycocoll (as a representative of amino acids) did not show any influence worth mentioning on σ and η.

Witte peptone (as representative of amino acids) did not show any influence worth mentioning on σ and η.

TABLE I.

σ (expressed in number of drops) of water (15° C.) = 53.2
η (" " " " seconds) " " (15° C.) = 198

		σ	η
Lime water (saturated)	---	53.4	—
" " "	+ Na_2S (5%)	54.1	—
Glycocoll	1% solution	54.6	191 –195
"	5% "	56.0	200--204
Witte peptone (W. P.)	0.1% "	62.9	192
" " "	0.25% "	65.8	192
" " "	0.5% "	67.2	194
" " "	1% "	69.2	202
Gelatin (7 days old)	0.1% "	55.2	209
" (7 " ")	0.25% "	57.2	240
Gelatin in lime water (2 days old)	0.005% "	53.4	—
	0.01% "	55.2	—
Witte peptone (W. P.) and gelatin (1 week old)	0.1 gel. + 0.1 W. P.	63.0	209
	0.1 " + 0.25 "	65.8	214
	0.1 " + 0.5 "	68.1	216
	0.25 " + 0.1 "	63.4	252

	σ	η	Total in N in 100 cc.	HCHO fig. for 100 cc.
Old lime	69.8	216—222	632.8 mg.	10.4
Med. lime	65.9	204—206	302.4 mg.	6.0
Another medium lime	65.8	201—204	257.6 mg.	5.4

Gelatin (as representative of most complicated splitting up product of collagen) showed only a small increase of σ (very di-

Digitized by Google

lute solutions are relatively more effective than strong ones), but a very considerable increase of η (the temperature is an important factor for η but not so delicate for σ).

Mixtures of Witte peptone and gelatin showed also the great influence of peptones on σ, their small influence on η and the little influence of gelatin on σ and its great influence on η.

Finally a few used limes were tested and the results of chemical tests compared with σ and η.

A stalagmometer was used for the experiments. The number of drops allowing the measurement of σ and the time necessary for emptying the tube allowing the measurement of η.

The figures in Table I illustrate the above.

Finally, it may be remarked that the work of Professor Stiasny: "Die Wirkungsweise der Kalkäscher" (*Der Gerber*, 1906) still remains the standard work on this subject. One of the results of this work indicates that the kations acting may be placed in the following order:

$$\dot{NH_4} \qquad \ddot{Ca} \qquad \ddot{Ba} \qquad \dot{Na} \qquad \dot{K}$$

in regard to their swelling and plumping action on skin, $\dot{NH_4}$ being weakest, $\dot{K}$ being strongest. The hair loosening action, on the other hand, is in exactly the opposite order, $\dot{K}$ being weakest, $\dot{NH_4}$ being strongest.

March 24, 1914.

MELTING POINT OF STUFFING GREASES.

By P. M. C. Armstrong.

I have had quite a few harness leather tanners ask me if I knew any way to determine roughly the melting point of stuffing greases. I have shown some of them the method we use here. Of course there is nothing new about it, but perhaps some of the lay members may find repetition useful.

Take a laboratory thermometer, graduated to the Fahrenheit scale, and dip the bulb in the melted stuffing, first having thrust it through a cork which will loosely fit in the neck of a florence

Digitized by Google

flask of 500 cubic centimeters capacity. A drop of grease is permitted to harden on the bulb, and it is then hung in the flask. The flask is then held in a pail of water at a temperature of 135° F., and the point noted when the grease becomes clear, and also when the bead drops off.

Care must be exercised not to let the air in the flask warm up too rapidly. This can be regulated by raising or lowering the flask in the pail. When the temperature comes within five degrees of the suspected melting point, it should be retarded so as not to heat at a greater rate than one degree per minute.

This method will, of course, not give the true melting point of the grease, but it has been found sufficiently concordant to regulate the stuffing mixture.

RECOVERY OF GREASE FROM BLEACHING TABLES IN HARNESS LEATHER TANNERIES.

By P. M. C. Armstrong.

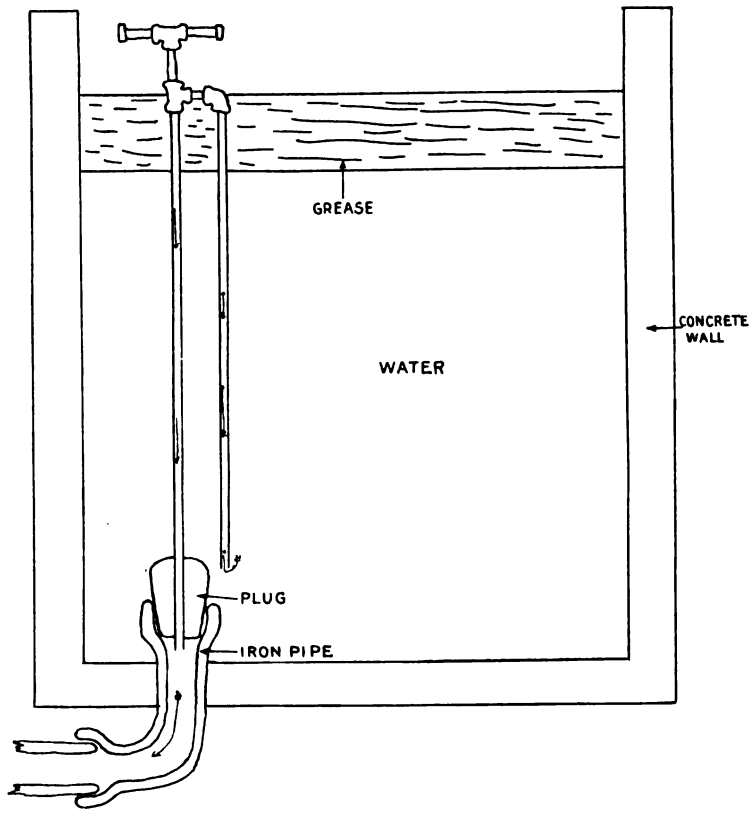
Many harness leather tanners nowadays finish leather on the flesh side by bleaching instead of whitening. That is, the leather is brushed on the flesh side with hot water, and the grease so removed is slicked off and run away, with the water.

Very few tanners make any effort to recover this grease, and much valuable material is lost in this way. It can easily be recovered, however, if desired, by means of a simple device. A pit is dug in the ground and connected with a sewer by means of a wrought iron ell which projects upwards into the pit. This is fitted with a hollow plug, into which is fitted a piece of three-quarter inch gas pipe, with a return, as shown in the accompanying figure.

The water will run off through the pipe and the grease will float on the top, where it may be skimmed off and melted up in a kettle, to be used over again. When the grease is skimmed off, the plug is drawn. Should the grease be left too long in the pit, through carelessness, it will get deep enough to run into the

Digitized by Google

gas pipe, and will plug the entrance to the sewer, and warning will be given by the pit running over.



The amount of grease which can be recovered by this simple device is amazing.

METHOD FOR CHROMIUM DETERMINATION IN LEATHER.

By Louis E. Levi and Aug. C. Orthmann.

The article by Mr. L. Balderston in the June, 1914 number of the JOURNAL of the A. L. C. A. on methods for chromium determination, is very timely, as it will tend to bring us one step nearer to the standardization of all methods used by chemists employed

Digitized by Google

in the leather industries. We describe below the methods employed for chromium determination in leather in the laboratories of the Pfister & Vogel Leather Co.

Nothing new or original may be found about the methods, but where accuracy and speed are the essential objects sought for in a large laboratory we find the methods thoroughly satisfactory in every respect. Where a large number of analyses are made daily on leather and where a complete analysis is necessary, although a short method for chromium may seem advisable the operator can be working on another determination while waiting for the development of the chromium result. This is one reason why we favor the methods which follow.

We note the method described by Mr. Balderston for chromium in leather. In a former article, this JOURNAL, October, 1911, page 469, we mentioned different fusion mixtures for fusing ash containing chromium and found that the mixture of equal parts of sodium and potassium carbonates was not satisfactory including a number of other mixtures with which we got unsatisfactory results. We finally found that a mixture of equal parts of sodium carbonate, potassium carbonate and borax glass gave good results and least trouble as far as sputtering was concerned. The above mixture will not creep up the sides of a platinum crucible nor will it sputter when heated intensely. The fusion is complete in from 15 to 25 minutes depending upon the amount of iron and aluminum present. The mass fused is easily soluble in hot water.

Where the ash determination is important, as we find it is, we see no great advantage in using the method as described by Mr. R. V. Tarshis in the June, 1914, JOURNAL, as by this method it would be necessary to make a separate determination of the ash.

The method described by us in which we use an iron crucible we consider rapid enough to answer most purposes and where a battery of 15 or more determinations are under way the whole can be completed in a very short time, 15 chromium determinations by this method can be made almost as rapidly as 5. Of course iron cannot be determined by this method, but this determination is not always required, the chief determinations being chromium and aluminum.

Digitized by Google

For many years we used for this purpose a wrought iron crucible the wall being about 1/16-inch thick and having a capacity of about 25 cubic centimeters. We found that this kind of crucible could not be used more than for 3 fusions, sometimes it could be used for 4 but never more. We then had a crucible made from a piece of steel shafting which was placed in a lathe and hollowed out to about 25 cubic centimeters capacity. This crucible was used for more than 2 years and at least 400 fusions were made with it, but as making crucibles like the one mentioned required a lot of time, we found it rather expensive. At the same time we found that cast iron would answer the purpose just as well as steel, so we had a pattern made and a large number of cast iron crucibles made with the following dimensions:

Inside diameter	1¼ inches
Outside diameter	1¾ inches
Height	1½ inches
Capacity	25 cc.

Beehive shape, flattened on the small end.

We find these cast iron crucibles can be used for about one year, daily, or for from 200 to 300 fusions. The cost of the crucible is about 3 cents each.

Ash.

Our methods are as follows:

Place 3 grams of the finely cut leather in a platinum, porcelain or alundum crucible, ignite until thoroughly ashed over a Bunsen burner or by placing in an electric furnace.

Chrome.

Remove the ash to the iron crucible and add about 3 grams of sodium peroxide. Pulverize the mixture to a homogeneous mass with a small glass rod taking care to brush all chrome off the rod into the crucible. Heat the mixture over a burner to a red heat and continue fusion for about 10 minutes; remove from flame and allow to cool. Then place crucible with fusion into a 500 cubic centimeter casserole and add about 300 cubic centimeters of distilled water and boil for from 15 to 20 minutes. Wash the dissolved fusion into a 500 cubic centimeter flask and cool under the tap. When cool dilute to the mark and mix well. Allow the iron precipitate to settle and filter off 100 cubic centi-

Digitized by Google

meters into an Erlenmeyer flask. Add cold dilute sulphuric acid in excess, then add 10 cubic centimeters of a 10 per cent. solution of KI and titrate with N/10 Hypo as usual.

In case iron and aluminum is to be determined use the following method:

Fusion mixture—1 part dry sodium carbonate
1 part dry potassium carbonate
1 part dry borax glass

The above mixture must be well pulverized and kept in well stoppered bottles.

Place the ash in a platinum crucible and add about 4 grams of the above fusion mixture and place over a Bunsen burner and fuse for about 15 to 25 minutes. When cool dissolve the fusion in water and acidify with HCl, add NH_4Cl and NH_4OH in slight excess. Boil for 5 minutes, then filter and wash filter with boiling hot water until free from chlorides. Dry the precipitate, ignite and weigh as Fe_2O_3 and Al_2O_3. Determine chrome in the above filtrate as usual.

We make this method public in the hope that other chemists in our Association will take this article as an incentive to give the members the benefit of their knowledge and experience in this class of analyses as well as others.

Milwaukee, Wis., June, 1914.

ABSTRACTS.

Experiments on the Oxidation of Sewage without the Aid of Filters. E. ARDERN and W. T. LOCKETT. *J. S. C. I.*, May 30, 1914, 523-39. Samples of raw sewage contained in bottles of 80 ounces capacity were aerated by drawing air through them with a filter pump until nitrification was complete. The time required was about five weeks. The sludge was then allowed to settle, the clear liquid decanted and a fresh portion of sewage introduced and the process repeated. Each time the length of time required to oxidize all the nitrogenous matter to nitrates decreased, until finally it was possible to oxidize a fresh sample completely within 24 hours. The authors call the deposited solids "activated sludge." It is necessary that the alkalinity of the sewage be rather more than sufficient to take care of the nitric acid resulting from oxidation of the ammonium compounds. In some cases this must be accomplished by adding a small amount of alkali. The activated sludge must be kept in intimate contact with the sewage during aeration. The volume of sludge

Digitized by Google

used for a given volume of sewage is an important factor in the rate of nitrification. The first 3 hours suffice to oxidize colloids, etc., producing a well-clarified effluent; the later stages consist in nitrifying the ammonium compounds. Attempts to divide the process into two parts, carbonaceous fermentation and nitrification, were not successful. The activity of the sludge deteriorates if fresh sewage is added before the nitrification of the former batch is complete. The activity of the sludge may be restored, however, by aerating it alone after the withdrawal of the partly purified sewage. The process of nitrification proceeds best at temperatures from 12° to 24° C. (55°-75° F.). Below 10° C. (50° F.) oxidation proceeds very slowly. The sludge settles out readily, is flocculent, dark brown and not offensive. After prolonged settling it contains 95 per cent. water. Counts on gelatine plates show up to 30 million bacteria per cubic centimeter. Analysis of the dry matter shows organic matter 65 per cent., mineral matter 35 per cent. The total nitrogen is 4.6 per cent., phosphorus pentoxide 2.6 per cent., matter extracted by carbon tetrachloride, 5.8 per cent. Preparations are being made to test out the process on the large scale. The high percentage of nitrogen in the activated sludge makes it probable that it can be utilized to advantage for fertilizer.

Research Work by Students of Tanners Institute, Pratt Institute, Brooklyn, N. Y. Published by the Institute. (1) *An Investigation of the Effect of Acids on Hides*, by WARREN E. MARVIN. Test tubes were partly filled with 20 per cent. gelatin jelly, slightly alkaline and colored with phenolphthalein. Five cc. of acid solution was poured on top of the jelly, and the depth of penetration, shown by decolorization of the jelly, measured each day. Formic, lactic, acetic, oxalic, sulphuric and hydrochloric acid were used, in N/5, N/10 and N/50 dilution. The penetration was greater in the case of the stronger solutions, but for a given strength there was no material difference among the different acids except that on long standing acetic penetrated farthest. Dilutions were also made on the basis of percentage of actual acid, 1 per cent., 0.5 per cent. and 0.1 per cent. being used. Here the penetration was roughly proportional to the normality of the solutions. Similar tests were made using saturated lime water for dissolving the gelatin. In this case the penetration of lactic and oxalic acids was less than the other four. The plumping effect of each of the six dilutions of all six acids was tested by immersing pieces of limed hide for 4 days, measuring their volume before and after. Results given in the table show percentage increase in volume after 4 days:

	N/5	N/10	N/50	1%	0.5%	0.1%
Formic	93.5	67.8	9.5	93.5	103.8	7.4
Lactic	79.7	76.9	7.7	79.7	78.8	4.0
Acetic	59.3	83.8	27.5	59.2	70.0	3.8
Oxalic	62.4	76.6	16.8	62.4	102.4	35.5
Sulphuric	54.7	61.3	13.5	54.8	55.6	69.3
Hydrochloric	69.0	81.0	13.1	69.1	102.4	62.7

Digitized by Google

2. *Depilating with Sodium Sulphide.* LEO A. MAUTNER. Analysis of a sample of commercial sodium sulphide showed 31.5 per cent. sodium sulphide and 17.2 per cent. sodium hydroxide. To a solution of 19 pounds in 400 pounds water, 4.75 pounds calcium chloride was added, to decompose the sodium hydroxide. A pack of hides unhaired in this solution was much less plump than hides unhaired with sulphide alone. Analysis showed 0.24 per cent. NH_3 in the used liquor, and 0.97 per cent. Na_2S, against 1.5 per cent. at the start. The liquor was made up to original strength and a second pack put through, after which the percentage of ammonia was found to be 0.70.

3. *Change in the Composition of Limes during the Process of Unhairing.* R. L. MOORE. (See paper by Dr. Allen Rogers in JOURNAL for January, 1914.)

4. *Soaking in Reference to Dissolved Hide Substance.* W. C. CHING. Experiments were carried out with a view of determining the amount of hide substance dissolved, the amount of water taken up by the hide, and the effect on the fat and ash content. The soaks used were distilled water, 5 per cent. salt solution, 1 per cent. sodium sulphide, 0.1 per cent. caustic soda, and 1 per cent. formic acid. Two kinds of hide were used, green salted cowhide and dry Chinese goatskin. Detailed results are tabulated and graphs drawn.

Chemistry and Analysis of Fats for 1913. W. FAHRION. *Zeit. angew. chem.* (*Aufsatz*), 1914 (I), 273-90. An exhaustive review with copious references. We select:

The fat constituents insoluble in the usual solvents, the reviewer has repeatedly designated as "oxydized fat." M. Tamura states that on evaporation of the petroleum ether solution no auto-oxidation of the unsaturated fatty acids ensues, but on drying the evaporated residue the I number falls off. The unsaponifiables are also especially sensitive, hence drying in a vacuum is preferable.—For measuring melting points, R. Meldrum places the material at unequal heights in a small U-tube and observes when the level is restored.—A. Bömer employs a new principle in distinguishing fats and detecting mixtures, namely, observing the difference between the melting points of the glycerides and the corresponding fatty acids obtained by saponification. For instance:

Tristearin	73.0	— 70.5	= 2.5°
α-Palmitodistearin	68.5	— 63.4	= 5.1°
β-Palmitodistearin	63.3	— 63.2	= 0.1°
Stearodipalmitin	57.5	— 55.7	= 1.8°

The acetin method for glycerin gives incorrect results according to Tortelli and Ceccherelli because a partial hydrolysis of the triacetin takes place on titrating back the excess of acid. The Hehner method is correct in principle but in practice too troublesome. The authors are working out a modified bichromate method. (The CrO_3 may be rapidly titrated through KI with thio.—Tr.).—Kreis and Roth to isolate and separate

Digitized by Google

high melting acids fractionally precipitate them in alcoholic solution with 10 per cent. of the theoretical Pb-acetate. The precipitation is decomposed with HCl, and the separated acid repeatedly recrystallized from alcohol. Or the fat may be saponified, acidified with acetic acid and then fractionally precipitated.—In this line Normann and Hugel note that in recrystallizing the acid from alcohol, prolonged heating may produce esters; further molecular mixtures may persist in some cases, hence change of solvents is needed.—Leiste and Stiepel's method for determination of colophony in fats and soaps depends upon the insolubility of ordinary Na-soaps in acetone while Na-abietate is soluble.—Hoepfner and Burmeister consider the Hübl method most reliable for the I number; the Wijs method gives figures increasing with the excess of reagent while the Hanus number increases rapidly with the temperature.—To distinguish animal and vegetable fats, Marcusson and Schilling, following Windaus, employ an alcoholic solution of digitonin (1 per cent.). Twenty cc. of this are shaken with 50 grams fat in a separatory funnel 15 minutes. The settled oil is drawn off, and the residue shaken and thoroughly washed with ether in which the digitonid is insoluble. It is then warmed with 1½ cc. acetic anhydride ½ hour and the acetate separating on cooling recrystallized from alcohol. Cholesterin and phytosterin acetates are distinguished by their m. p.—G. Tellera detects vaselin in lanolin by precipitation with ⅓ volume absolute alcohol added to the ether solution.—Wool fat stearin contains 9-30 per cent. unsaponifiable, m. p. 41.5-59°, according to E. Coen.—Five per cent. mineral oil in wool-fat olein will give a cloudy solution in 4 volumes of a mixture of amyl and ethyl alcohol (1:2).—Opinions vary as to the value of reduced oils for soap making. There is but one German firm (Oelwerke Germania at Emmerich) producing hardened oils in quantity, 250 to 500 tons per week (Normann patent). Whale oil is the raw material and the following products are marketed:

	Melting point	Price (Aug. 1913)
Talgol	35-40	70-71 M.
Talgol extra	43-47	71.5-72.5
Candelite	48-50	73-74
Candelite extra	50-52	74.5-75.5
Krutolin		66.5-67.5

The last is soft, a lard substitute. Linolith is a new brand, m. p. 45-55°. W. J. K.

Unsaponifiable Constituents of Natural and Hardened Fats. J. MARCUSSON and G. MEYERHEIM. *Zeit. angew. chem.* (Aufsatz), 1914 (1), 201-3. A sample for analysis designated beef tallow, because of its high iodine number (64.8) was suspected to be a hardened fat similar to "Talgol." Nickel could not be detected, but Bömer has shown that it is only retained when free acids are in the original natural oil; moreover other metals are used as catalyzers. On treatment of the fat with

Digitized by Google

alcoholic digitonin solution (method above) pure cholesterin was obtained indicating a foreign animal fat. The "inner" iodine number of the fat was found to be 111, indicating fish oil, since that of land animals does not exceed 100 (beef tallow 89); Talgol gives 107. This last being so high indicates that in hardening, the oleic acid is mostly reduced, while a portion of the more unsaturated acids remains unhydridized.

A quantitative determination of the sterins in various natural and hardened oils was made by the digitonin method.

	Total unsaponifiable %	$[\alpha]_D$	Sterin from digit. %	%	Unsaponifiable sterin free $[\alpha]_D$	I no.
Whale oil, brown.....	1.8	+ 1.9	0.15	1.6	0.0	64.6
Beef tallow	0.3	—12	0.03	0.2	—12	—
Castor oil	0.3	—15.8	0.13	0.13	+ 5.7	—
Hardened oils:						
Talgol	0.9	— 1.9	0.10	0.7	+ 1.3	56.1
Talgol, extra	0.9	— 3.3	0.07	0.7	—	—
Castor oil	0.3	—10.1	0.13	0.19	+ 5.2	—

It is seen that the sterins are not the chief constituents of the unsaponifiables as often assumed, but 33-55 per cent. with vegetable oils, 8-14 in animal oils. The unsaponifiable residue freed from sterins (and excess digitonin) is generally semi-solid, consisting of alcohols with some hydrocarbons in the case of whale oil. The iodine number of the sterin free portion varied from 56-78. Accordingly the method of Thoms and Fendler for detecting small amounts of mineral oil in linseed oil, which depends upon the determination of the iodine number of the unsaponifiables, may also be used for the other fatty oils; the total unsaponifiable containing the sterin must have about the same number as when sterin free (pure sterin = 68). It was found that the sterin content of natural fats is progressively lowered on hardening; whale oil, I number 114; talgol extra, m. p. 38, I number 38, sterin 0.07 per cent.; candelite extra, I number 13, m. p. 45, sterin 0.02.

The analyses in the table show that the sterins are partly altered on hydridizing the fats and alteration products of the phytosterins were actually separated in the case of the vegetable oils, but failed with the animal oils. The lesser stability of cholesterin was shown by direct experiment. Pure cholesterin was reduced at 195° in presence of nickel by Adamla's process and yielded about 25 per cent. dihydrocholesterin. Reduced at 250° a resinous product was obtained from which nothing definite could be separated, and which no longer gave the cholesterin (digitonid) reaction. Phytosterin similarly treated was unaltered at 200° and at 250° only 8 per cent. was precipitated by digitonin; the main product appeared to be a solid hydrocarbon, m. p. 102-3°.

W. J. K.

Sulphite-Cellulose Lye as Tanning Agent and its Detection in Leather. J. H. SCHULTE (Fabrik Cellulose Extract "Excelsior"). *Ledertechn.*

Digitized by Google

Rundschau, 1914 [6], 129-32. This paper is further designated as "Remarks on the Article by Dr. Moeller (abstr. ante p. 246).

If Yocum and Faust conclude that cellulose extract in mixture with other tanning extracts reduces their tanning power by causing loss of tans, this contradicts all practical experience and the cellulose extract experimented with must have contained besides other alkalies fixing tannin also large amounts of lime or free mineral acids. No such loss occurs with Excelsior extract. In reference to cost of cellulose extract as a tanning agent, this should be based not on the hide powder analysis but on the amount taken up by hide in properly conducted tannage using nearly the entire extractive matter. Computing this way the writer makes quebracho cost 69 Pf. per kilo (in tans) and cellulose 33 Pf. in substance effecting tannage. Good cellulose extract is therefore about half as dear as quebracho and has the advantage of shortening the tannage and utilizing the untreated quebracho. The experiments of Prof. Sody (this JOURNAL, 1912 [7], 373) represent laboratory conditions and not the slow progressive system of the practical tannery. As to Dr. Moeller's experiments, the result that impregnated cellulose may be partially washed out again is to be expected and applies also to quebracho or other tanning extracts. That the water extract for experiments 4-6 gave no reaction for cellulose extract commends it. "What more does the tanner wish than for the extract to stay in the leather?" The principal thing with cellulose extract as with any other is to apply it properly. W. J. K.

Sulphite-Cellulose Extracts as Tanning Agents. PAUL GULDEN. *Ledertechn. Rundschau,* 1914 [6], 105-7. A reply to Moeller's article (ref. above) as a matter of fact large amounts of cellulose extract are being consumed by tanners which is the real test. Mistakes may occur now and then, and there are some inferior extracts, but when a good brand like the "Saxonia" (made in the writer's factory) is used good leather is produced. W. J. K.

Estimation of Free Sulphuric Acid in Leather. J. PAESSLER. *Ledertechn. Rundschau,* 1914 [6], 153-6. The author has demonstrated the destructive action of this acid upon leather by specimens of known history. The grain becomes brittle, cracking on bending, and with age the entire leather breaks like pasteboard. The deterioration increases with the amount of the acid and especially with heat so that the evil effects result sooner in warm regions. The author does not agree with Eitner (*Gerber,* 1907; abstr. this JOURNAL, 1908 [3], 65) that small amounts are fixed by the organic components of the leather and as in the case of wool, are harmless. Free sulphuric acid should be entirely excluded from leather, especially such as is to be long stored.

The sources of this acid in leather are from its employment in: (1) pickling, (2) plumping, (3) deliming, in all of which the acid may not be entirely washed out; further (4) its occasional addition (oftener

Digitized by Google

SO_3) to tan extracts; (5) use in bleaching leather; (6) in dyeing with acid aniline colors; (7) in blacking and currying leather.

Reviewing the methods proposed for the determination of the free acid, that of Jean, extracting with alcohol, gives much too low results. Procter and Searle (*Leather Trades Review*, 1901, Jan. 9) ignite the leather with a known amount of soda, and titrate with acid; the difference represents free SO_3 after correcting for the natural alkalinity of the ash as determined by a blank test. This method proved unsatisfactory in the Freiberg laboratory. Nor can Kohnstein's method (abstr. JOURNAL, 1911 [6], 603) be recommended; it is very indirect and has many sources of error. Balland and Maljean's method with its various improvements (Paessler, Sluyter, Arnoldi, Meunier) is useful, but the computation by difference is subject to the united errors of two observations. Rehbein's method of combustion in oxygen (abstr. JOURNAL, 1913 [8], 304) is more direct, but errors accumulate in computing the SO_3 from dissociated sulphates. Finally the determination in general is affected by sulphur from such sources as thiosulphate used to assist tannage, or from such substances as the new Neradol D, or the sulphonated oils used in currying. The author's dialysis method (abstract, ante, p. 243) is next described. Quantitative experiments show that after 24 hours, 20 to 30 per cent. of the actual amount of acid present went into the dialysate. A variety of leathers of known content of free sulphuric acid were tested and gave the following percentages reckoned on the assumption that 25 per cent. of the whole was extracted:

Actual content	Per cent. found	Difference
0.12	0.16	+ 0.04
0.25	0.22	— 0.03
0.49	0.39	— 0.10
0.74	0.59	— 0.15
0.98	0.64	— 0.34
1.22	1.03	— 0.19
1.84	1.93	+ 0.09
2.45	2.45	0.00

Further improvements in the process and apparatus are being studied.

W. J. K.

Sulphuric Acid in Leather. *Technikum.*, June 6, 1914. The title of this paper is "Second Session of Commission 15 (on Leather Testing) of the German Association for Testing Technical Materials." The meeting was held in Berlin, February 25. Four matters were considered: (1) Testing of leather for sulphuric acid. (2) When is the use of sulphuric acid objectionable? (3) Is the use of sulphuric acid in the making of leather to be prohibited under all circumstances? (4) Are all other acids to be prohibited? In regard to point (1) (see preceding abstract), the commission decided to postpone action, awaiting further development of Dr. Paessler's dialysis method. Decision on point (2)

Digitized by Google

was postponed until the settlement of (1). In regard to question (3), it was feared that the elimination of sulphuric acid from the processes of leather manufacture would result in increasing the price of the product. The following resolution was, however, adopted: "In the present state of our knowledge, free sulphuric acid appears hurtful to the durability of leather. It is possible to make bark-tanned grain leathers without the use of this acid, and probably without any increase in cost. This must result in natural tan colored leathers and beet leathers coming into the market somewhat darker in color than at present. It is recommended that the use of sulphuric acid in the preparation of bark-tanned grain leathers be debarred." Decision on point (4) was also postponed. The matters assigned to the next session were (1) rules in regard to the use of the various sorts of tanning materials, and (2) qualitative tests for particular materials. L. B.

The Preservation of Hides and Skins for Export. ANONYMOUS. *Bull. Imp. Inst.*, 12, 106-110. A table is given of the quantities and values of hides imported into the United Kingdom during the years 1910, 1911, 1912. The total values were 4,270,000, 3,750,000 and 5,650,000 pounds sterling for the 3 years. The best methods are also given for preparing and preserving the hide for shipment. ALEX. F. FUERST.

Government Inspection of Wattle Bark in South Africa. ANONYMOUS. *Bull. Imp. Inst.*, 117. The Government of the Union of South Africa have decided to undertake from and after April 1, 1914, the inspection of wattle bark prior to its shipment. The official grades are as follows: H. 1, Heavy (first class); H. 2, Heavy (second class); M. 1, Medium (first class); M. 2, Medium (second class); T. 1, Thin (first class); T. 2, Thin (second class); B. G., Below Grade. Standards for the different classes will be fixed by the Government and the grading be made in accordance. ALEX. F. FUERST.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. IX AUGUST, 1914 No. 8

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1914, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR. W. H. TEAS. H. C. REED. J. H. YOCUM. F. H. SMALL. H. T. WILSON. J. H. RUSSELL. F. P. VEITCH. } . . . Past Presidents

OFFICERS, 1913-'14

PRESIDENT—W. K. ALSOP, Ridgway, Pa.
VICE-PRESIDENT—C. W. NORRIS, 80 South Street, New York, N. Y.
SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y
LLOYD BALDERSTON, Ridgway, Pa.
C. R. OBERFELL, Harrisonburg, Va.
T. A. FAUST, 323 Academy Street, Newark, N. J.

CHANGES OF ADDRESS.

A. W. Cappon, to 156 West 12th St., Holland, Mich.

F. M. Dupont, to 11334 Church St., Morgan Park, Ill.

DIED.

George D. Callender, an active member of this Association, died at St. Luke's Hospital, Chicago, July 5, 1914. He was a native of Scotland. His chemical education was obtained at Leeds University under Procter. He came to this country in 1910 in the interest of Röhm & Haas and at the time of his death was their Chicago representative.

Digitized by Google

THE REHBEIN METHOD OF DETERMINING SULPHURIC ACID IN LEATHER.

By W. J. Kelley.

The article by Rehbein in *Collegium,* No. 518, p. 300 (1913), on "The Determination of Free Sulphuric Acid in Leather by Burning in a Stream of Oxygen in a Combustion Tube,"* furnished the basis for the work taken up in this thesis.

Between two and three grams of ground or finely cut leather is weighed into a porcelain or platinum boat and placed in a combustion tube about 60 centimeters long and about 1.8 centimeters in diameter. A gasometer or tank of oxygen is connected through a drying train to one end of the tube. About 12 centimeters from the other end is placed a platinum spiral about 10 centimeters long inside of which is a mixture of platinized quartz and quartz similar to that used in the Dennstedt elementary analysis. Through contact with this substance complete combustion of the gases is accomplished. The boat containing the leather is placed about 8 centimeters from the contact mass. Just in front of the rubber stopper at the end of the tube is placed a wad of glass wool in order to prevent any small particles of the ash from being driven into the absorption solution. The observation that small particles of the ash were carried along was noted only when the leather was treated with alkali sulphates to determine whether or not they were broken up by the burning of the leather. When it was burned alone these particles were not to be found in the glass wool. The rubber stoppers at either end of the tube are protected from the radiated heat by pieces of asbestos paper placed over the tube. The products of combustion are led into a water-cooled absorption flask containing distilled water into which about 1 gram of Na_2O_2 is put. A 300 cubic centimeter Fresenius absorption flask was found to give good results.

The combustions are run in an ordinary combustion furnace, or, better, in a Dennstedt furnace. The quartz is brought up to a brightly glowing heat while a slow stream of oxygen is passed through. When this point is reached then commences the

* See abstract, this J., 1913, p. 304.

Digitized by Google

burning of the leather. Care must be taken at this point to have a lively stream of oxygen passing so that complete combustion of the leather and the gases will be accomplished and no explosive puff will result. If the combustion cannot be started by the heat radiated from the burners under the contact mass then the end of the boat nearest the catalyzer should be heated carefully, stopping at the first flash because then the burning will go on of itself. After all the leather has burned the boat is heated vigorously its full length to set free all the SO_3 of any of the sulphates in the ash.

When the combustion is completed, the absorption solution is heated and acidified with HCl and the sulphates precipitated and determined in the usual way with $BaCl_2$.

Before this method can be used to determine the free H_2SO_4 in leather one must first determine the amount of the acid resulting from the burning of the hide-sulphur. For this, a vegetable tanned leather which had never been treated with H_2SO_4 is burned and the resulting acid fixed and determined. In each determination of the free acid this amount must be subtracted from the total acid found and the fixed acid from the remainder to give the result desired.

EXPERIMENTAL DATA.

As has been said, the object of this work is the study of the method proposed by Rehbein, duplicating, if possible, his work in order to determine its practicability as a laboratory method for the determination of free sulphuric acid. Rehbein's account of his work as given in the article already quoted, was followed as closely as possible and in the succeeding pages is given a detailed account of the actual conditions encountered.

Samples were first made up to contain a definite known amount of H_2SO_4. To do this, a leather was used which had never come in contact with sulphuric acid during the process of manufacture. A weighed amount of the leather cut into strips was placed in a porcelain evaporating dish and a known amount of standard N/8 acid was added. After allowing the leather to soak in this for some time the acid was poured off, the dish carefully washed into a graduated flask and the solution made up to volume. An aliquot portion of this solution was titrated with

Digitized by Google

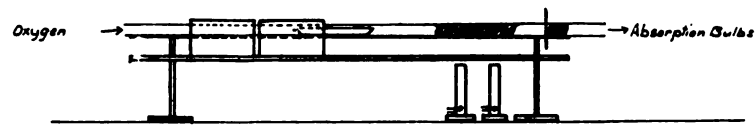
standard N/4 sodium hydroxide solution, using phenolphthalein as the indicator. Ten grams of NaOH were dissolved in water and made up to a liter. Standardization against N/2 HCl showed it to contain 0.009449 gram per cubic centimeter NaOH. An N/4 H_2SO_4 solution was made up and standardization against the NaOH showed it to contain 0.01294 gram per cubic centimeter H_2SO_4. One cubic centimeter of the NaOH is equivalent to 0.01157 gram H_2SO_4. From the titrations of the acid in which the leather is soaked the amount of alkali required by the whole volume, one liter, is calculated and converted to grams of H_2SO_4. This is the amount of acid not taken up by the leather. Subtracting this from the amount of H_2SO_4 known to have been added gives the amount of acid taken up by the leather from which the percentage is calculated. Samples containing 0.79 per cent., 0.61 per cent. and 0.52 per cent. were made. These samples were dried at about 50° to 60° C. for three or four days and then the strips were cut up by means of a circular saw thus getting the leather in a finely divided state. It was kept in glass stoppered bottles.

A furnace as is employed in Dennstedt elementary analysis was used for the combustions. The tube was about 60 centimeters long and 1.6 centimeters in diameter. The oxygen necessary for the combustions was provided by a gasometer which was filled by heating a retort containing a mixture of MnO_2 and $KClO_3$ (1-8). The gas was passed through a train of purifying towers containing concentrated sulphuric acid, calcium chloride and soda lime. About 12 centimeters from the outlet end of the tube was placed a platinum spiral about 10 centimeters long packed with platinized asbestos, 4 grams and platinized quartz, 2 grams. The assumption was that the asbestos, furnishing greater area than the quartz and capable of filling the tube more completely, would prove more effective than the platinized quartz and quartz which Rehbein uses. Between the catalyzer and the end of the tube was placed a wad of glass wool. To protect the rubber stopper in the end of the tube a piece of asbestos paper was put over the end of the tube.

The first run was made with the catalyzer mentioned above. About 8 centimeters from the contact substance was placed an

Digitized by Google

alundum boat containing the charge of finely divided leather. The oxygen was run through the tube at a moderate rate, while the catalyzer was brought up to glowing by the heat of two No. 5 A Meker burners. The asbestos covers were left off the tube over the boat keeping it cool. After pure oxygen had begun to come through the tube as evidenced by the bursting into flame of a glowing splinter, the absorption apparatus was attached. This consisted of a 200 cubic centimeter Fresenius absorption flask containing distilled water in which about one gram of sodium peroxide had been dissolved. The oxygen supply was then increased from a speed which would just allow the counting of the bubbles passing up through the sulphuric acid to a slightly more rapid rate.



The covers were placed over the part of the tube containing the boat and the heat caused to radiate towards it. After a time there was a flash across the top of the leather in the boat. Then the mass began to burn with a dull glowing at the end farthest from the source of heat. This continued until the whole charge was consumed along the length of the boat. After the combustion was completed the boat was heated by means of a Bunsen burner to break up any sulphate that may have been held in the small amount of ash remaining. After allowing the oxygen to run through for about five minutes longer it was stopped and the absorption flask detached.

This was emptied into a beaker and the flask carefully washed out, the washings being added to the original solution. This was diluted and heated to boiling and then acidified with concentrated C. P. HCl. The solution, which was slightly yellow, now became colorless. Hot dilute barium chloride solution was added slowly and with stirring, and the precipitate formed was allowed to settle. This was set aside to stand over night in a warm place after which it was filtered and washed free of chlorides, ignited wet and weighed.

Digitized by Google

Boat + Charge	8.1750 gr.	Crucible + $BaSO_4$	14.7880 gr.
Boat	6.2874 gr.	Crucible	14.7552 gr.
Charge	1.8876 gr.	$BaSO_4$	0.0328 gr.

$$\frac{0.0328}{1.8876} \times \frac{98 \times 100}{233} = 0.73 \text{ per cent.}$$

0.73 per cent. H_2SO_4 found in sample
0.52 per cent. H_2SO_4 actually in sample

The boat was removed from the furnace and heated to redness and another charge placed in it. A second combustion was run under identically the same conditions as in the preceding one. Here the absorption solution contained many small black particles which were removed by filtration after acidification. This time after the pale yellow alkali solution was made acid it turned a slightly darker yellow. The SO_3 content was determined as before.

Observing that in the first run the gases passed through the alkali solution very rapidly and suspecting the possible escape of some of the SO_3, a second absorption flask was connected to the first one. On making acid and adding $BaCl_2$ a white precipitate of $BaSO_4$ was noted. Hence, in the following comubstions for the Fresenius absorption flask was substituted a Meyer bulb tube (six bulbs) which, it is reasonable to believe, would be more efficient, allowing, as it does, a longer period of contact between the gases and the absorption solution.

Boat + Charge	8.9552 gr.	Crucible + $BaSO_4$	14.8010 gr.
Boat	6.2872 gr.	Crucible	14.7532 gr.
Charge	2.6680 gr.	$BaSO_4$	0.0478 gr.

$$\frac{0.0478}{2.6680} \times \frac{98 \times 100}{233} = 0.76 \text{ per cent.}$$

0.76 per cent. H_2SO_4 found in sample
0.52 per cent. H_2SO_4 actually in sample

Another run was made without making any changes in the apparatus. The oxygen supply and method of ignition of the charge and the burning of it were as nearly as it was possible to do, exactly the same. This time, on acidifying the absorption solution it turned from a pale yellow to a decidedly dark yelow. The $BaSO_4$ was precipitated, filtered, washed, ignited and

Digitized by Google

weighed as before. This time the result was much lower than those of the previous two combustions which checked closely.

Boat + Charge	8.5086 gr.	Crucible + $BaSO_4$	14.7838 gr.
Boat	6.2858 gr.	Crucible	14.7532 gr.
Charge	2.2228 gr.	$BaSO_4$	0.0306 gr.

$$\frac{0.0306}{2.228} \times \frac{98 \times 100}{233} = 0.57 \text{ per cent.}$$

0.57 per cent. H_2SO_4 found in sample
0.52 per cent. H_2SO_4 actually in sample

This combustion was made with a charge weighing 2.5352 grams, no change being made in the apparatus or the method of conducting the combustion. When the yellow alkali solution was washed from the bulb tube to a beaker and the boiling solution acidified the color changed from the yellow to a pale red which became darker and darker until finally it was so dense as to appear almost black. This was accompanied by the separation of black, carbonaceous matter, so much so that it was considered useless to precipitate the SO_3. The solution possessed a strong phenolic odor which probably resulted from the presence of pyrocatechol or like compounds which result from the decomposition of tannins. The red color was probably due to the presence of phlobaphenes. Many tannins are resolved, on heating with acid, into dextrose and gallic, or ellagic acid, or an amorphous red coloring matter or phlobaphene. Phlobaphenes are soluble in alkali solutions but are with difficulty soluble in weak acid solutions.

These conditions, without doubt, indicate the incomplete combustion of the leather. This might result from two things: insufficient oxygen supply or the inactivity of the catalyzer. Inasmuch as the oxygen supply has been practically the same throughout the runs and the first combustions gave high results it might be concluded that the fault, under these conditions at least, is not so much with the oxygen supply as with the catalyzer. From the gradual decrease in the results of the consecutive runs and the increasing intensity of the color of the absorption solution due to the coming over of organic bodies not broken up it is evident that the catalyzer had gradually become deadened or inactive. At the same time, the fact that some

Digitized by Google

smoke has been driven over into the absorption bulb in all of the runs would tend to indicate that the stream of oxygen passing through was too rapid, *i. e.*, the products of the combustion were swept through the catalyzer at such a rate as to prevent complete combustion.

Hence, the catalyzer was removed from the tube before the next run and it was heated highly in a porcelain crucible to revivify it. Before this heating, when held in a stream of illuminating gas the catalyzer showed no change. After the heating it glowed brightly under the same conditions.

The next run was made with a charge of 2.4080 grams using the revivified catalyzer, the positions of the boat, catalyzer, etc., being the same as before. In accordance with the assumption regarding the oxygen supply reached in the last run, the gas was caused to pass more slowly through the combustion tube. The rate of flow was such as to allow the bubbles to be very easily counted as they came through the acid. The supply was not fast enough to permit the ignition of the charge by radiated heat. Therefore, heat was applied directly to the boat and this had to be maintained through the whole ignition to accomplish complete combustion. It was found that the slight amount of red, gummy matter which condensed in the cold end of the tube in all but the first two of the previous runs had greatly increased in this run. There was also a greater amount of smoke leaving the leather and passing through the tube than in previous runs. The acidification of the absorption solution resulted in the same conditions as experienced in the run immediately preceding this one, a dark red solution and the separation of carbonaceous matter. It was considered useless to precipitate with $BaCl_2$ in this case also. It is evident that at this time the other extreme had been reached in regard to the oxygen supply and that it was now too slow.

The catalyzer was again taken out and revivified as before and the tube cleaned free of the gummy matter in the end. The catalyzer and charge were replaced in the same relative positions. This time a slightly faster stream of oxygen such that the bubbles coming through the acid could just be counted, was used. Again the heat had to be applied under the charge before it started to burn. In every case the combustion has been at the

Digitized by Google

end nearest the oxygen supply which, if it is fast enough, will maintain the burning without heating. Here the heat had to be applied throughout the combustion. This time the absorption solution was perfectly clear and colorless on acidifying. The sulphuric acid content was determined as before. The condensation of the dark red matter in the cold end of the tube was again noted. This showed another case of incomplete combustion.

Boat + Charge	9.0550 gr.	Crucible + $BaSO_4$	14.7746 gr.
Boat	6.2850 gr.	Crucible	14.7523 gr.
Charge	2.7700 gr.	$BaSO_4$	0.0223 gr.

$$\frac{0.0223}{2.7700} \times \frac{98 \times 100}{233} = 0.34 \text{ per cent.}$$

0.34 per cent. H_2SO_4 found in sample
0.52 per cent. H_2SO_4 actually in sample

With the idea that if the catalyzer was heated more highly, better and more complete combustion could be obtained, more heat was applied to the contact mass until it was glowing very brightly. The same rate of oxygen supply was maintained as before and the combustion was started and kept up by the application of heat directly to the boat as before. The absorption solution showed a rather darker yellow than the preceding run. The sulphuric acid content in it was determined in the usual manner. From the result obtained it is evident that this change has made no difference, the gummy matter being found in the end of the tube again.

Boat + Charge	8.6912 gr.	Crucible + $BaSO_4$	14.7930 gr.
Boat	6.2846 gr.	Crucible	14.7746 gr.
Charge	2.4066 gr.	$BaSO_4$	0.0184 gr.

$$\frac{0.0184}{2\ 4066} \times \frac{98 \times 100}{233} = 0.31 \text{ per cent.}$$

0.31 per cent. H_2SO_4 found in sample
0.52 per cent. H_2SO_4 actually in sample

The catalyzer, without being revivified, was heated still more highly in this run to see if the life of the catalytic action would be lengthened if the contact mass was kept at a higher heat. The oxygen supply was kept the same as in the two preceding runs and the heat was also applied to the charge directly but, as in all

Digitized by Google

previous cases, very gradually. The charge was 2.1970 grams. This time the absorption solution changed from a yellow to a very dark red on acidification and, hence, was rejected.

Thus, it is seen that with each successive run the combustion is more and more incomplete due to the failing of the catalyzer regardless of the heat at which it is kept.

The first two of this series check well but are much lower than the actual percentage of H_2SO_4 present. Here, we have had a moderate stream of oxygen and direct heating of the sample. The inference to be drawn is that the direct heating drives out the volatile matter faster than will allow its complete oxidation. But since there is no other remedy than direct heating when a moderate supply is introduced it seems that a swift supply of oxygen is necessary.

It would be reasonable to suspect that the matter condensing in the cold end of the tube would be not only an evidence of poor combustion, but that it would also act as an absorbent for some of the SO_3 passing through it. To verify this suspicion the end of the tube was soaked in C. P. nitric acid which was then evaporated off and the residue taken up in distilled water with a little hydrochloric acid added. $BaCl_2$ solution added to this showed a decided white precipitate, thus affirming the presumption that the condensed matter was an evil as well as the sign of one.

The original assumption that the greater area provided by the platinized asbestos would make it more efficient than the quartz seems to have been contrary to fact judging from the results obtained. Hence, the same catalyzer as used by Rehbein was placed in the tube in precisely the manner prescribed by him in his article. About equal amounts of platinized quartz and bits of quartz tube were placed within the platinum spiral, filling the tube. This was brought to a bright glowing and then the heat was radiated along to the boat containing the charge. As Rehbein directs, the stream of oxygen was slow at first and then when the heating of the charge was begun, the oxygen supply was increased causing a lively stream to pass through the acid of the purifying train. The combustion started of itself after the heat had been very gradually directed towards the boat from the con-

Digitized by Google

tact mass. It needed no external heat to keep the charge glowing. After it was completely burned the alkali solution was transferred to a beaker, diluted, boiled and acidified and the now familar signs of incomplete combustion were again in evidence, the solution turning a very dark red. This was rejected as no accurate results could be hoped for if the $BaSO_4$ precipitated under such conditions.

From the preceding run it would appear that the platinized quartz and quartz alone did not act with any great degree of efficiency. In the next run the platinized quartz was carefully revivified by heating for a long time at a high heat in a porcelain crucible. The platinized asbestos used in previous combustions was subjected to like treatment. The entire amount was placed in the tube as the contact mass, the quartz filling the 10 centimeter platinum spiral and the asbestos placed next to it towards the outlet end of the tube. The contact mass was kept a little nearer the end of the tube than heretofore in order to keep it just hot enough, if possible, to prevent the condensation of any organic matter. This end was accomplished during the combustion, but there is danger of the introduction of an inaccuracy in the form of sulphur compounds from the rubber stopper which may be heated too highly. The contact mass was heated to glowing with a slow stream of oxygen flowing and then the supply was increased until it bubbled through the acid just a little faster than would allow the counting of the bubbles. The heat was gradually deflected to the boat and eventually ignition was accomplished and the mass glowed at the end until the whole mass was consumed. When the combustion was complete the absorption solution was treated in the usual manner. Its color was a clear pale yellow which became colorless. The sulphuric acid was determined as usual.

Boat + Charge	8.5524 gr.	Crucible + $BaSO_4$	14.7795 gr.
Boat	6.2852 gr.	Crucible	14.7520 gr.
Charge	2.2672 gr.	$BaSO_4$	0.0275 gr.

$$\frac{0.0275}{2.2672} \times \frac{98 \times 100}{233} = 0.51 \text{ per cent.}$$

0.51 per cent. H_2SO_4 found in sample
0.52 per cent. H_2SO_4 actually in sample

Digitized by Google

The next two runs were made in an attempt to determine the amount of SO_3 resulting from the burning of any sulphur that may have been in the leather. A portion of the original sample containing no acid was used. After the catalyzer had been taken out and revivified it was replaced in the tube, this time a little farther back from the end of the tube to avoid melting the stopper by the excessive heat. The same oxygen supply as used in the preceding run was fixed as near as possible when the burning of the leather started. The charge could not be caused to begin to burn by the radiated heat so heat was very gradually and carefully applied by means of a Bunsen burner. The leather did not burn readily and the heat had to be kept under the boat to finally consume the whole charge. The result of this run was the changing of the absorption liquid to a dark red solution containing black organic matter and also the condensation of organic matter in the end of the tube.

A second run was made exactly duplicating this one, but for the fact that the oxygen was run a little faster. There was no difference in the results obtained.

In a final endeavor to get complete combustion the tube was filled with catalyzing material to the extent of about 25 centimeters. There was the platinum spiral and about 15 centimeters of carefully revivified platinized quartz and quartz and about 10 centimeters of new platinized asbestos. This was placed about 6 centimeters from the end of the tube and about 10 to 12 centimeters from it was placed the charge. The distance between the charge and contact mass was thus increased because the nearness to such a large mass of glowing hot material might result in the too rapid heating of the charge by radiation at the beginning. A lively stream of oxygen was caused to pass and although the heat from the burners under the contact mass was deflected towards the charge it only charred and could not be caused to burn until a burner was placed beneath it after which the black mass began to glow dully. This was kept until the whole mass was consumed. Acidification of the absorption solution caused it to change from a rather pronounced yellow to a pale pink which, on standing, grew deeper in color until it was almost black. This

Digitized by Google

was rejected as being worthless as far as a determination was concerned.

Thinking that perhaps the charge of leather, which was of necessity packed rather firmly into the boat as it was very light and fluffy, was in too compact a mass, another run was made in which the leather was very loosely packed within the boat. The catalyzer was removed and revivified and replaced as before in the same amount and in the same position. The heat was radiated along from the contact mass with a lively stream of oxygen flowing. The charge ignited of itself after it had charred to a hard black mass. Then the end nearest the oxygen supply began to glow and this continued until the whole had been consumed. The ash contained in the boat was subjected to high heat to break it up as was done in all combustions before. The absorption solution was a clear pale yellow which on acidification became a pale pink. Hot dilute $BaCl_2$ solution was added slowly and with stirring and the precipitate allowed to stand over night. After filtering, washing and igniting the $BaSO_4$ was weighed.

Boat + Charge	7.3632 gr.	Crucible + $BaSO_4$	14.7720 gr.
Boat	6.2850 gr.	Crucible	14.7518 gr.
Charge	1.0782 gr.	$BaSO_4$	0.0202 gr.

$$\frac{0.0202}{1.0782} \times \frac{98 \times 100}{233} = 0.32 \text{ per cent.}$$

0.32 per cent. H_2SO_4 found in sample
0.52 per cent. H_2SO_4 actually in sample

DISCUSSION OF RESULTS.

In an analysis of the results of the Rehbein method a point most worthy of note is the fact that the first two runs check each other very closely, being 0.73 per cent. and 0.76 per cent., and that the results of other runs fall far below these and at the same time do not check each other with any degree of consistency. Owing to the impossibility of determining the SO_3 resulting from the combustion of the sulphur originally present in the leather, if such is the case, an accurate judgment as to accuracy of the results is impossible. But, considering the fact that Rehbein found the leather used by him to yield 0.18 per cent. SO_3 from the sulphur present it might be presumed that the

Digitized by Google

leather used here contained an amount approximately equal to this. If such be the case, then the first two runs would be the most accurate, giving close to 0.50 or 0.54 for the percentage of H_2SO_4 contained in the sample. If this assumption is false, of course these results could not be considered accurate, but it is the author's opinion that there is good reason to believe it true.

In all probability the proper conditions for efficient combustion were hit upon at first, but all efforts to duplicate these later failed. It is of importance to note that at this time the catalyzer was new, never having been used before. This may have been one cause for the high results. But, under the same conditions after the contact substance had been carefully revivified as advised by Sudborough and James in their book "Practical Organic Chemistry" the same results could not be obtained.

The difference in the condition of the catalyzer would in all likelihood make a difference in the oxygen supply and temperature at which the catalyzer should be maintained. Working on this principle the oxygen supply was varied from a very slow stream to a very rapid one and the contact mass was heated from a point where it barely glowed to the highest heat possible, but it is evident that just the exactly proper conditions required were not hit upon as Rehbein did.

It is to be realized that the method of ignition of the charge is an all important one, another point that must be regulated to a nicety. Rehbein advises the heating to be very gradual with a "lively" stream of oxygen flowing. It was found that when such was attempted that before the charge was actually ignited the organic compounds distilled out of the leather were swept along through the tube at such a rate as to prevent proper combustion. Also when the charge was ignited and glowed brightly in the brisk flow of oxygen the combustion was entirely too rapid, smoke being swept into the absorption bulb and at such a rate as to entirely preclude any chance for the assumption that efficient absorption was being effected. When a slower stream of oxygen was run the sample would not burn of itself, but had to be heated throughout to secure complete combustion and when it did burn there was evidently not enough oxygen for complete combustion.

Digitized by Google

It is very evident that condensation in the cold end of the tube and its subsequent absorption of the SO_3 passing through it is a very bad feature of the combustions. To eliminate this there must be either complete combustion or the end of the tube must be kept so hot as to prevent the condensing action. In case the former could not be effected the latter could be made possible by eliminating the rubber stopper entirely by drawing the tube out and bending it to fit directly into the absorption apparatus. Thus heat could be applied to this portion of the tube without fear of driving sulphur-containing decomposition products of rubber into the absorption solution.

These troubles suggested a change in Rehbein's method of procedure which could not be worked out at this time, but which would seem to promise an improvement. It would make the method still more like the Dennstedt method for the determination of sulphur in organic compounds. That is, the fixation of the SO_3 would be by a suitable agent within the tube at a proper distance from the catalyzer. In the Dennstedt method lead peroxide is used, but it is believed that soda lime could be used instead. This should be kept at a low temperature to prevent the condensation of organic matter in it. It could then be removed, dissolved in water, acidified, filtered if necessary, oxidized with Br water and the sulphate determined as usual with barium chloride.

CONCLUSIONS.

The Dennstedt method for elementary analysis has been proven conclusively to give accurate results with proper manipulation. But it must be borne in mind that the charge used in this is about 0.2 gram and although the Rehbein method is based upon it there seems to be a fundamentally weak point in the latter procedure inasmuch as a charge about 15 times as great is used. The proper manipulation of the Dennstedt furnace itself is acquired only after much practice, there being innumerable niceties of adjustment that come only with experience. Hence, the manipulation of the Rehbein method where the experimental conditions are even more difficult due to the relatively great charge,

Digitized by Google

3 grams, requires such a skill as would militate against its adaptation to ordinary commercial laboratory practice.

WORCESTER POLYTECHNIC INSTITUTE,
June, 1914.

FORTY YEARS AGO.*

By Prof. Henry R. Procter.

The Editors of the Year Book have suggested as a subject for an article for the Year Book: "Reminiscences of Leather Trades Chemistry for forty years back."

It is somewhat difficult to write reminiscences of what did not exist, and it is hardly too much to say that in the "Seventies" leather chemistry was as yet unborn! It is true that some of us were interested in the possibilities of tannin analysis;—that "hardy perennial" of our branch had its root much earlier, in the work of Sir Humphrey Davy, who precipitated tannins with gelatine, and attempted to wash, dry, and weigh the coagulum, with results which were interesting and to some extent comparative, but which would hardly appeal to our extract-making friends, either as regards accuracy or high percentage. Before the time of which I write, this root had thrown out some quite promising shoots. There was Mulder's method of volumetric precipitation with a standard gelatine solution which, even in its most improved form failed to give any result at all with many materials; and there was Gerland, who used a solution of Tartar Emetic instead of gelatine with scarcely better results, and there were various notions with lead and zinc and copper, which would work sometimes!

The first ray of real light was the publication (about 1870) of Löwenthal's permanganate method with indigo-carmine, which really gave sharp results, though, as we later discovered, many added precautions were needed before any two investigators could rely on concordant analyses; and it afforded no comparison of different tanning materials, though for different samples of the same, its results in its later improved forms were quite reli-

* Leather Trades' Year Book, pp. 89-94.

Digitized by Google

able, and even now for many purposes of tannery control it is one of the best methods.

Among the very early processes for tannin estimation was that of Hammer, who took the gravity of a tannin solution before and after treatment with hide-powder; and following on this came the Muntz & Ramspacher "tan-tester," in which filtration through a piece of raw hide was substituted for the use of hide-powder.

In those days, hide-powder was not obtainable commercially, at least in a state of sufficient purity to give reliable results, and the "tan-tester" even in fairly careful hands could not be trusted within about 10 per cent.; but when the chemists of the Vienna Research Institute succeeded in producing a really good hide-powder; substituted evaporation and actual weighing for the somewhat difficult and uncertain gravity determination; and, at the suggestion of the present writer, introduced filtration instead of mere maceration with the hide-powder, we had for the first time a really practical method of determining the relative tanning strength, though not always the commercial value of the various materials.

The adoption of chromed powder, and the substitution of shaking for filtration is in the memory of all of us but it may not be out of place to recapitulate the reasons for what at first sight looks like a backward change. In order to secure complete and sufficiently rapid detannization of the stronger tannin solutions originally used by the Vienna chemists, it was necessary to use the hide-powder in successive portions, since the white powder is not absolutely insoluble even in quite cold water; and in warm weather, putrefactive changes were liable to set in during the time necessary for maceration. Thus the filter, which automatically brought the detannizing liquid in contact with fresh and untanned layers of the powder, and so caused very rapid detannization, was a real improvement and simplification; but when the Americans showed that the insolubility and permanence of the powder could be advantageously increased by chroming; and the time of maceration reduced by shaking to a period even shorter than that required for filtration, while that the powder could be finally washed free from the traces of solu-

Digitized by Google

ble hide substances always produced during drying immediately before use, and the somewhat uncertain error always introduced in the filter method by these solubles practically reduced to *nil*; and further that the errors produced by unequal packing of the filter and slight variations in the powder were largely avoided, it became evident that a still further advance in accuracy could be made.

Even the claim that *any* good powder could be used without affecting the results was justified so long as the accuracy possible with the filter was regarded as sufficient, but with the much greater exactness obtainable with the shake method, even the small differences, (usually less than 1 per cent.) caused by different powders have become important, and a still better concordance will be obtained when the arrangement has come into force that all English chemists should work with an identical powder.

Improvements are no doubt possible, but the writer ventures to think that the time is still distant when the use of hide-powder will be superseded, since it does measure the actual weight of tanning substances absorbable by hide; and any more strictly scientific process will have to be preceded by methods for the separation and identification of the different individual tannins.

Turning from the analysis of tanning materials to the still more important chemistry of the tanning process itself, one may say that however imperfect our knowledge is to-day, it is vastly in advance of that of 40 years ago. In the case of sole-leather, deliming before tanning was practically unknown, and but little attention was paid to the complicated chemical changes of the suspenders, which were frequently allowed to become quite limy, with the consequent production of stains and bad color, which often only became obvious when the goods were dried, and were attributed to quite other causes. Probably the present writer's limewater method of acid determination did much to lessen this ignorance, and at least it indicates with accuracy the danger-point as regards limestains, though it gives little information about the plumping powder of the liquors.

With our present limited knowledge, there is indeed no possible complete solution of this question, since the swelling is the

Digitized by Google

result of a complicated balance of osmotic pressures, dependent not only upon the acids but the salts and tannins which are present; but recent work on the acid swelling of gelatine and hide fiber has at least thrown light on the conditions of the problem. With regard to the still more difficult question of the action of acid in dressing leather tannage, the greatest advance we have made is to recognize that the question exists, and, as was pointed out years ago by Kathreiner, is one of prime importance.

Forty years ago, the view mostly prevailed that the tanning process was a case of chemical combination between the hide and the tannin, as suggested by Davy; and Knapp's work, though published in 1858, was little known, at least, in England. Knapp believed that the process was one of simply coating the unaltered fibers with deposits from the tanning liquors, or, as the popular phrase now goes, was one of "adsorption." The controversy is perhaps not yet ended, though the arguments on both sides are changed. The probability is, as is so frequently the case, that there is truth on both sides. There can be little doubt that in the early stages of tanning, important chemical changes of the fiber do take place, governed by equilibria similar to those of the swelling process, while the later stage is largely one of deposition of solid matters on and between the fibers. It is likely, as the conditions of these two separate processes become more fully understood, that both may be rendered more rapid, and that cheaper materials than the decomposition-products of tannins may be used for the filling and solidification which is the main object of the final stage.

Forty years ago vegetable and alum tannages and chamoising and their combinations were the only leather making processes in practical use. Chrome, aldehydes, and synthetic tannins were quite unknown; and though a perfectly practicable chrome process had been discovered by Knapp 20 years earlier, its value had not been recognized. These newer processes have not only opened a wide field for the chemist and enforced his value on the practical tanner, but have thrown much light on the true theory of tannage, and will themselves prove guide-posts for the chemist to new and undiscovered methods.

Digitized by Google

Turning back to the limeyard and the wet-work generally, our knowledge of 40 years since was scanty indeed. Bacteria, which we now recognize as the most important agents, were then as good as undiscovered; and sulphides were only known in the form of arsenic limes, though a few cranks were working with gaslime and tankwaste, and Bottger's calcium sulphide was mentioned as a curiosity in the text books. The really active agents, chemical and bacterial, in bates and puers were first investigated by Wood at a later date. There is still very much that we do not know; and we have not even adequate methods for limeyard control, and no complete theory of alkaline swelling and its repression; but at least we have some conception of the problems to be solved, and the exact knowledge will come in time.

I fear I have very imperfectly pictured our ignorance in the seventies, and perhaps spoken too optimistically of our present knowledge; but the immense advance from then to now is incontestable, and I cannot conclude the article without a tribute of respect to the men to whom it is due. Some of these are fortunately still with us, and it is right that they should know that their work is not forgotten, but too many have passed into the beyond. Of the latter we may mention Kathreiner, whose most important work has never been published, but whose stimulating and encouraging influence can never be sufficiently appreciated by those who have not known him. Then there was Andreasch, who even in the last stages of consumption continued to work at the problems of bacteriology and plant-structure for which he did so much, and there were von Schroeder, and his colleague Councler, and the younger von Schroeder and Boegh, and, alas many others who if they had lived might have done great things.

Of our still active members it would be invidious to speak by name, but one may be allowed a tribute to the retired veteran Eitner, who with his able assistants did so much to bring the importance of science to the notice of the trade, and whose own writings are marked by a combination of scientific knowledge and practical acumen which render then still a storehouse of useful ideas.

Digitized by Google

COLLOIDAL TANNINS.*

By M. C. Lamb.

Scientists have for many years drawn a distinction between substances which have the power of diffusing through a semi-permeable membrane and those which will not; the former are termed crystalloids and the latter colloids. Use has been made of this in practical toxicology (the analysis of poisons). When it is desired to ascertain whether a metallic poison like arsenic, mercury, lead, etc., is present in the stomach of a dead person, the contents of this are placed in a parchment-covered tray floating on water; this tray being semi-permeable the crystalloidal substance (compounds of arsenic, mercury, etc.), diffuse through the membrane, and are tested for in the solution upon which the parchment tray floats.

Colloids in contact with their specific solvents are, generally speaking, plastic substances of a gelatinous character, whereas crystalloids have the power of crystallizing, and include the more common chemical salts; there are few chemical salts which however cannot be obtained in a colloidal state.

The hide itself is a colloid, and the vegetable tannins are colloidal in character, whereas mineral tanning substances may be either crystalloidal or colloidal. This property, to a certain degree explains why the diffusion of a solution of a vegetable tannin, say oak bark, through pelt is so very much slower than the diffusion of a crystalloid like potassium dichromate. The hide being a colloidal gel through which a colloidal solution passes with some degree of difficulty.

The phenomena of the colloidal condition of matter are, as yet, only partially understood, but differences of colloidal condition no doubt account for the variability of the rates of diffusion of the various vegetable tannins. An example of this, which will be fully recognized by the practical man, is the relative rates of tanning of quebracho wood and oak bark. The former contains a proportion of 7 parts tannin to 1 part non-tannin; the latter 7 parts tannin to 4 parts non-tannin. As is well known the quebracho penetrates through the pelt with considerably greater

* Leather Trades' Year Book, 1914, pp. 127-29.

Digitized by Google

rapidity than does oak-bark, particularly when used in dilute solutions. Owing to the relative amount of dissolved non-tannin substances in the oak bark solution the latter is more colloidal in character and hence diffuses more slowly.

One very important requirement to successful tanning is the recognized necessity for placing green pelt into solutions which are "mellowed," in order to prevent the liability of bringing about the defects known as "drawn grain," or "case hardening," which result when untanned pelt is placed into too strong solutions of a new tanning material. In practice, a weak "mellow" liquor which has been used for a very considerable number of packs of goods and has been "worked down the yard" is used in the early stages of tanning. This liquor is of a much less astringent character than when freshly prepared, owing to the absorption from the solution by the preceding packs of goods which were in a more advanced stage of tannage, of the astringent tannin which is more readily taken up by the partially tanned goods; and the gradual accumulation of a greater proportion of the non-tannin matters which are less easily absorbed. In the ordinary "first liquor" the proportion of the non-tannin substances to the tannin substances is very much greater than in freshly prepared solutions. Further, the much used liquor contains a proportion of dissolved hide substance and lime-salts, in a colloidal condition. It will be evident therefore from these examples that the colloidal condition of the tannin matter has a very important bearing on the subsequent behavior of the solution.

Developing from the work of my friend Mr. C. F. Cross, of Messrs. Cross & Bevan, who found when experimenting with that colloidal substance extracted from vegetable seeds, and commercially known as Tragasol, that when this complex was mixed in varying proportions with tannic acid and tanning extracts a curdy precipitate was formed in which the combination took place in approximately the ratio of their formula weights; and noting the peculiar behavior of this highly colloidal substance and the manner in which it precipitated gelatine, the writer was asked to collaborate with a view to the practical application of the substance as a tanning agent.

The highly complex colloidal bodies which result from such

Digitized by Google

combinations present the following general characteristics. They are insoluble in water, but readily mix with it. On heating the mixture it becomes a continuous and transparent solution with a great increase in viscosity. These colloidal bodies are peculiarly adapted as tanning agents because of the fact that the transition to the insoluble condition by combination with the pelt in skin substances is comparatively slow.

It has been found on making an enormous number of experiments on a small practical scale, that, as was to be expected from a survey of the theoretical conditions involved, owing to the highly colloidal condition of say a mixture of an astringent tanning agent like quebracho, and tragasol in the required molecular proportions to effect the combination, it is possible to place the goods after deliming direct into as concentrated a solution as it is convenient to make, and without any addition of water beyond that contained by the pelt itself, without the slightest liability of bringing about drawn or "case hardened" grain. Moreover, it is possible, owing to the restraining effect exerted by the tragasol complex upon the astringent tannin to use the substances in such strengths as to complete the tannage of sole butts in as short a space of time as 30 hours; and it is no doubt possible to shorten the time even further if it was considered necessary, or advisable.

The mixture is best applied in the drum owing to its gelatinous character which prohibits its being used in the paddle. Leather tanned by this method is free from the common defects produced by the usual drum tannage with extract, particularly in regard to the water-resisting character of the product. This is due to the insoluble nature of the tragasol-tannin complex, which reduces to a minimum the amount of water-soluble matter in the tanned leather. The color of the leather is excellent, due no doubt primarily to the fact that there is little oxidation and also to the peculiar slow drying property possessed by the tanned leather, owing to the tragasol-tannin complex parting with its absorbed water with extreme slowness.

Where desired, the tannage, first commenced with the colloidal tanning agent can be completed by the use of liquid extract in

Digitized by Google

an undiluted form; the grain having been fixed with the tragasol-tannin complex the partially tanned leather presents no difficulty to the penetration of the stronger tanning extract.

THE PRACTICAL INTERPRETATION OF ANALYTICAL RESULTS.*

By John R. Blockey.

Much time and attention have been devoted in recent years by leather trades chemists to the methods of analysis of the materials used in leather manufacture. Reference has only to be made to volumes of the *Collegium,* or the JOURNAL of the American Leather Chemists' Association, to see what a great proportion of the total research work has been directed to the perfecting of the methods of analysis.

Whilst correct methods of analysis are essential and as a basis on which to build any superstructure of chemical control of the processes of leather manufacture, they should be regarded as a means to an end rather than the end itself. Correctness of analytical methods is useless if the interpretation of the results cannot be truthfully carried out. The trend of recent discussions, particularly with regard to the question of tannin analysis seems to suggest that chemists have rather obscured the value of the analytical results in an attempt to devise methods which will give absolutely uniform results with different analysts.

If this method is carried to the extreme, that is, if an analytical method is sought or modified so that it will give absolutely uniform results without keeping in view the practical interpretation of the result it will be easy to obtain methods which are completely out of harmony with practical behavior.

The search for methods which give uniform results applies of course to empirical methods such as the hide powder method of tannin analysis rather than to the strictly stoichiometric methods as, for instance, the analysis of a deliming acid.

The question of tannin analysis perhaps presents the most points of interest in this connection. No method of analysis has had so many vicissitudes. It has certainly monopolized the

* Leather Trades' Year Book, 1914, pp. 103-11.

Digitized by Google

major portion of research work and discussion which have been carried on by leather chemists.

Most of the discussion and research work has been devoted unfortunately to the question of uniformity of result rather than to the elucidation of the connection between the laboratory result and the practical behavior.

Because such an analysis, by slight alterations in the methods of manipulation, can give such different results, it is not to be wondered at that different classes of experimenters will favor different methods. Those interested in the selling of the material will favor methods which give higher results, whilst those who are interested in the buying, will favor the ones giving low results.

Even now, when methods have been devised which will give remarkably uniform results, we find that different analysts favor quite different methods. That the method can be made to give quite uniform results if always carried out in exactly the same way, is fairly well agreed upon. Oma Carr[1] has furnished striking proof of this in connection with consignments of extracts. In the case of 33 cars of powdered chestnut extract, the extract was invoiced on the analysis of Chemist A, and the contract providing for adjustment on the average analysis of Chemist A and Chemist B. Comparing the 33 sets of analysis made by both chemists only twice was there a greater difference than 0.5 per cent. The average difference being about 0.2 per cent. The total averages of both chemists were identical. This example shows the uniformity possible in a commercial transaction.

If the production of a method which gives uniformity of results without taking into account the practical interpretation, is insisted on, then tannin analysis will be useful in a limited sense. It will be almost useless to compare one extract with another. Its main purpose will be to check deliveries of one extract, as in the example quoted.

As an example of the different methods favored by different analysts, we may mention the use of the filter bell method of analysis by the Continental chemists and the German extract

[1] *Journal American Leather Chemists' Asscciation*, 1914, p. 139.

Digitized by Google

manufacturers, and the use of the shake method by the English and American chemists. The filter bell method gives, as a rule, rather higher results than the shake method (about 2 per cent. on a material 30 per cent. of tannin). The shake method is favored because it gives more uniform results with different analysts. The Continental chemists favor the filter method because[2] "it is much more practical and simple than the shake method . . . . . it furnishes results which are comparatively more exact . . . . ." Incidentally, of course, the filter method is favored by sellers of tanning materials because of the higher results.

On the other hand, we have H. G. Bennett[3] proposing that the present shake method should be altered, so that the results will be still lower in tannins than at present. He maintains that by the present shake method of analysis, materials are represented as tannins when they are really non-tannins, and that the tanner is not getting anything like the percentage of tannin indicated by the official analytical reports.

Apparently the only reason for supposing that some of the non-tannins are represented as tannins is that by suitably varying the conditions of analysis the proportions of non-tannins can be made to increase. He claims that he has devised a method so that the percentage of tannin are reduced by about three or four per cent. This is achieved by varying such factors as, a decreased acidity of hide powder, using less hide powder, detannization in more dilute solutions. Why a higher non-tannin and consequently on a lower tannin figure should be desired is not very evident. If a lowness of the tannin figure alone is desired, the writer could suggest ways and means by which it could be reduced to vanishing point.

The Value of the Non-Tannins.—What is wanted is evidently a clearer knowledge of the connection between the analytical result and the practical result. The main trouble seems to depend on the question: What is tannin and what is non-tannin? At present, despite recent researches which partially solve the problem of the constitution of the tannins, there is no sharp line

[2] U. J. Thuau, *Le Cuir*, 15th March, 1914.

[3] *Shoe and Leather Reporter*, 19th March, 1914.

Digitized by Google

of demarcation between tanning matter and non-tanning matter. The only definition is that supplied by the present method of analysis. Any substance which by the official method of analysis is not absorbed by hide powder is called non-tannin, and the difference between the amount of this and the total soluble matter is tannin.

Whether these so-called non-tannins have actually any tanning power in practice is not known conclusively.

The kowledge of the exact behavior and function of these non-tanning matters in practice would be extremely valuable, and time spent in search and discussion of this knowledge would be much more profitable than discussing errors of a half per cent. by different manipulators using different hide powders.

Having devised a method which will give reasonably uniform results, such as the present official methods of the I. A. L. T. C. and of the American Leather Chemists' Association, this might be adhered to and investigations carried out on a practical scale to see how far these results are borne out in practice.

To attempt to arrive at the connection between the analytical and the practical results, the conditions under which the analysis is made, and the practical conditions under which a material is used, might be compared.

The first and main point in this connection will be the non-tannins. In the analysis the hide is in excess whilst in practice the tannin is always in excess. This would tend to produce an analytical result too low in non-tannins, and therefore too high in tannins, if the practical tannage were carried out in such weak liquors as are used in analysis. With a large excess of hide there is a greater chance of removing every trace of matter which will combine with the fiber than there is in practice. On this point, therefore, the analytical result is likely to be too high, but practical tanning is never carried out in such weak solutions, and in such a way that only matters which actually combine with the fibers are removed from the liquors. In practice, liquors of such a strength are used that a great proportion of the total matter taken up by the hide from the liquor is not combined with the fiber, but is capable of being washed out again by water. This uncombined matter may reach up to 25 per cent.

Digitized by Google

or more of the total weight of leather. The amount of uncombined matter may be higher than the amount actually combined.

The following figures show the analysis of a typical heavily-tanned sole leather.

		Per cent.	
A.	Moisture	14.0	
B.	Hide fiber	30.1	Actual leather substance
C.	Combined tannin	27.1	Actual leather substance
D.	Matters soluble in water	28.1	15.8 tannins; 12.3 non-tannins
E.	Mineral ash not included in D	0.7	
		100.0	

This uncombined matter is largely composed of what would be called by the analytical method, non-tannin, and it is therefore not true to say that it is only the matters which are absorbed by hide powder which go to form leather. It would be nearer the truth perhaps to say that the tannin as measured by analysis gives the proportion of the material which will unite with the fiber.

Even with what is regarded as a very light tannage, the amount of uncombined matter may reach 10 per cent., of which nearly half will be so-called non-tannins.

The value of the non-tannin will vary more or less with the method of tanning, and generally speaking the heavier the tannage, *i. e.*, the stronger the liquors that are given, the more likelihood there is of the non-tannins being utilized. Of course the above remarks only apply to the addition of weight to the leather and not to the quality.

The value of the non-tanning matters in the liquors, with regard to the formation of acidity, or the mellowness of the liquors is a much more complex subject. To arrive at the true value of the non-tanning matters would entail considerable work and would vary for each material. Work carried out on the lines adopted by Dr. Parker and the writer some time since, in which chestnut extracts were detannized and the resulting non-tanning matters added in varying proportions to the original extract and leather tanned in these different mixtures, would lead to interesting and valuable results.

The Question of Blending.—Another point of variation be-

Digitized by Google

tween the analytical and the practical results is the question of blending. In analysis a material is used alone, whereas in practice very rarely are "single" liquors used. The mixing of two materials might cause variations in each, they may have mutual action upon one another in such a way that a non-tannin matter may become a tanning matter or *vice versa*. Simple experiments on this point could be carried out by making analyses of single materials, and also of blends, and determining if in the blends the total tanning matter was equal to the sum of separate tanning matters. This influence of blending will also be in evidence in connection with the amount of insoluble matter. This point is referred to later.

The Question of Acidity.—In analysis the liquor is made and analyzed immediately, and the acidity of the liquor is only what might be termed the natural acidity. In practice, liquors are allowed to stand, fermentation takes place and the acidity increases. Acid is also often added directly to the liquors. The effect of this acidity on the absorption of the tanning and non-tanning matters may be considerable.

The Question of Insoluble Matter.—Another great point of difference between the analytical and the practical results is the amount of insoluble matter. As a rule the analytical result will give a lower percentage of insoluble matter than is actually borne out in practice. This is especially the case with raw materials, such as barks, but is also true in the case of extracts. This difference is due mainly to two things, the fineness of division and the concentration of the liquor. The effect of concentration on the solubility is very marked and generally speaking, the higher the concentration the greater the proportion of insoluble matter, although this is not necessarily the case. In analysis the strength of the liquor is less than a half per cent. of tannin. The difference between this and some of the liquors used in practice is enormous and may produce variations in the amount of insoluble matter.

With solid materials the fineness of division before extraction varies in analysis and in practical working. The greater fineness of division for analysis will allow a more complete extraction of the soluble matter.

Digitized by Google

The temperature of extraction may differ also. In analysis the final extraction is always made at a temperature of boiling water, whereas in practice this may not be so. Here again the effect is to cause the analysis to err on the right side.

The tanner, who for instance buys chopped mimosa bark, and who has no system of hot water leaching, must not expect to extract the total amount of soluble matter as measured by the official method. The latter is rather to be looked upon as giving the maximum amount than can be extracted.

The Deposition of Insoluble Matter.—Even if the tanner succeeds in extracting the whole of the soluble matter it is not certain that he will utilize it all. Clear infusions of most materials will, on standing, gradually deposit insoluble substances. If the insoluble matter, *e. g.*, bloom, be deposited in the leaches, it is lost. Even if it reaches the liquors in which the leather is, most of the deposited bloom will be lost. Only the bloom which is actually deposited on the fiber is likely to be of service in the production of leather. Some materials, such as valonia are much more liable to this form of loss than others, such as mimosa bark, and in this connection extracts have an advantage over raw materials. Comparing an extract and a similar raw material which are equal in price per unit of tan the extract should prove to be cheaper in use.

The effect of blending materials may cause variations in the amount of insoluble matter. The constituents of one material may render soluble some of the insoluble portions of another material or *vice versa*.

As an example of this may be cited the case of the new tanning material Neradol D. According to researches by Grasser, Neradol D. has the property of rendering soluble some of the insoluble "reds" of quebracho extract. By analyzing mixtures of the two extracts and comparing with the separate analyses it was found that the mixtures contained much less insoluble matter than the separate materials. Neradol has the same property in conjunction with gambier. If a small quantity of Neradol be added to a turbid infusion of gambier an immediate clearing will be observed.

The Value of Insoluble Matter.—It is usually held that in-

Digitized by Google

soluble materials are useless in leather formation, but after the researches of Dr. Sommerhof on the tanning effects of insoluble substances it may be that a revision of this opinion will be necessary. Dr. Sommerhof produced leather entirely by means of insoluble substances such as freshly precipitated phosphates and silicates of the heavy metals. If insoluble colloidal inorganic materials will produce leather it is likely that the insoluble organic reds or phlobaphenes will also produce leather. If this is so, then the present conception of the value of the insolubles in such materials as quebracho and gambier must be changed. The common practice of rendering quebracho extracts completely soluble would seem also to be unnecessary.

Temperature of the Liquors.—In analysis the liquors are cooled down to atmospheric temperature before use, whereas in practice the liquors are occasionally used warm. The difference in temperature between analysis and practice may produce an appreciable difference in the amount of insoluble material, *e. g.*, a gambier extract may show, say, 4 per cent. of insoluble matter at 17° C. and only 1 per cent, at 50° C. In this case analysis shows less than is actually available.

In the foregoing consideration an attempt has been made to connect the analytical result with the practical result in the case of tanning materials. It was hoped to continue this line of thought to other things such as leather, oils, chrome liquors, etc., but sufficient trespass on the Editor's space has been made.

In conclusion it might be stated that the conditions are never as simple in practice as might be expected from analysis. The effect of concomitant circumstances must be allowed for in the interpretation of the analytical result, *e. g.*, the estimation of the amount of acid in a deliming liquor takes no account of the extent of ionization of the acid or of the amount of neutral salts, both of which factors modify the deliming action of the acid. Also in the usual analysis of one-bath chrome liquors (reduced bichromate) no account is taken of the organic products, but merely the ratio of chromium to acid. In the estimation of the amount of dissolved hide substance in lime liquors no distinction is made between the nitrogenous products arising from the hair

Digitized by Google

and epidermis, and that from the actual leather forming substance.

These cases illustrate the contention that correctness of analytical methods should not be the end but rather a means to an end.

BOOK NOTICES.

THE LEATHER TRADES' YEAR BOOK, 1914. This publication replaces the Tanners' Year Book of previous years. The honorary editors are M. C. Lamb and J. Gordon Parker. It is published for the United Tanners' Federations by the Anglo-American Technical Co., Ltd., 112 Tower Bridge Road, London, S. E. The price is 3 shillings, postpaid; cloth bound, 5 shillings.

Of the 210 pages, the first 37 are taken up with particulars in regard to the Federations, lists of officers and members, etc., with many portraits. Pages 38-40 embrace the report of the Central Committee of the United Tanners' Federation. The report of the Committee of the Light Leather Trades' Federation covers pages 41-7. Statistics of imports and exports are given, pages 48-74. A list of hide markets registered, with trade-marks, covers pages 75-87. Special articles as follows fill the remaining pages:

Forty Years Ago. H. R. Procter.
The Value of Scientific Training to the Leather Manufacturer. E. Stiasny.
$y = f(x)$. Cecil G. Williamson.
The Practical Interpretation of Analytical Results. John R. Blockey.
The Prospects of Leather Manufacture in China. J. Dyson Withinshaw.
The Worshipful Company of Leathersellers. C. E. Parker.
Colloidal Tannins. M. C. Lamb.
A Few Advantages to the Leather Trade of the Federations. F. S. Goulding.
The New American Tariff. E. S. Grover.
Imported Leather. A. R. Bennett.
The Russian Leather Industry. "An Exile in Russia."
Collodion in Leather Finishing. C. A. Higgins.
Some Remarks on Liming. J. T. Wood.
The Work of the Chemist in a Chrome Tannery. R. Faraday Innes.
The Measurement of Leather. G. A. Schettler.
A Tale of a Tail. Stanley G. Lutwyche.
The National Association of Tanners of America. John E. Wilder.

Digitized by Google

The Danish Leather Industry. Max Ballin.
The Heavy Leather Industry of Holland. J. L. Van Gijn.
Pure Salt and Its Value to the Leather Industry. Andrew Turnbull.
The Board of Agriculture. R. Stephenson.
Water Treatment by Permutit. L. H. Harrison.
The Hide, Leather and Allied Trades Society. Norman Green.
On the Desirability of a Little Judicious Skepticism. Douglas J. Law.
Analysis of East Indian Tanned Goat and Sheep Leather. M. C. Lamb.
Power from Spent Tan. C. E. Parker.
Progress of Science Applied to the Leather Industry in 1913. J. T. Jackson.

CHEMICAL REAGENTS: THEIR PURITY AND TESTS. Authorized translation of the second edition of E. Merck's "Prüfung der chemischen Reagenzien auf Reinheit." D. VanNostrand Company. 199 pages, 6 x 9 inches. $1 net.

This second edition follows the first in most respects. Many substances are discussed which were not included in the first edition. Each substance is described, and if it is used in several forms each form is described. Tests for all impurities likely to be present are given. There are abundant references, and where special apparatus is necessary it is clearly described. The solutions most used in analysis are put in a separate list and their preparation described. The book is well indexed, and nothing seems to have been left out which could help to make it acceptable to the research chemist or to any chemist who must test his reagents.

ABSTRACTS.

Filipinos Adopting Occidental Footwear. J. F. BOOMER, correspondent, Manila. *Daily Consular and Trade Reports.* The Philippine Islands afford a growing market for the sale of leather and the manufactures thereof. The imports from abroad in this commodity and its manufactures increased $195,942 between 1911 and 1913. The increase was made up principally of boots and shoes imported from the United States. This gain in the importations does not, however, represent the total increase in the use of leather and its manufactures in the islands. In recent years there has been an astonishing increase in the number of boots and shoes worn in the country.

The rising generation of Filipinos who are educated in the public schools are disposed to discard the native "chinela" worn by their parents and to adopt the leather shoes of American and European design. There

Digitized by Google

are upward of 600,000 pupils in the public schools. These as they reach the higher grades in the schools, as a rule, begin to wear shoes. Consequently, the market for shoe leather is expanding as the number of pupils in the schools grows. This expanding market is supplied to a large extent by local manufacture. There is one shoe factory in Manila, established by an American, using modern machinery and methods of manufacture. This factory maintains three retail stores in Manila for the sale of its product.

In addition to this there are a great many shops in which shoes and boots are made by hand by Chinese and Filipino cobblers. These hand shops find it more and more difficult to compete with the machine-made shoes; for in spite of the rapidly growing market, their wares do not sell readily when machine-made shoes are available. This is due to the fact that the younger generation of Filipinos are insisting more upon styles in shoes. As a rule the hand shop turns out a nondescript shoe, with no regard to the prevailing styles. Again, the hand-made shoe is usually manufactured from locally tanned leather, carabao hide principally, which retains a more or less offensive odor, and does not make a desirable shoe. Most of the small dealers who formerly sold hand-made shoes altogether now handle the imported article, or the product of the local factory, and cater to a more discriminating trade.

Sponges from Leather. *Leather Trades Rev.*, June 17. I have seen a great deal of leather which unintentionally bore a very striking resemblance to sponge, but the idea of disposing of leather waste by making it into artificial sponges is new. The process, as described by the *Revue de Chimie Industrielle,* is as follows: The leather waste, preferably from sole leather, is degreased, very finely shredded, and mixed with liquid rubber. This forms a paste which, when filled with pores, is capable of holding a large quantity of water in a similar manner to a sponge. In the manufacture of the sponges, 30 to 80 parts of the finely shredded and degreased leather fibers are saturated with thick milk of sulphur and dried. After drying, the fibers are immersed in a mixture of from 20 to 70 parts by weight of liquid rubber and ammonium carbonate, which coats them and forms a resistant mass, which is then moulded to the shape required of the finished sponges. The mass is then heated in a vacuum, first at a low temperature, and gradually raising the temperature to 260°-300°. This causes the decomposition of the ammonium carbonate, evolving gas which during its escape from the mass results in the formation of a great number of pores and cavities in the mass. The rubber of the mixture becomes vulcanized by the sulphur with which the leather fiber was treated, and acquires the necessary elasticity. Any gas which may have failed to escape from the interior of the mass is liberated, after cooling, by pressing the sponge against a surface covered with fine needle-points, and, finally, the sponges may be colored any desired shade.

Digitized by Google

The Estimation of Tannin in Cider. C. W. SPIERS, University of Bristol. *Journal of Agricultural Science,* January, 1914; *Collegium,* June, 1914, pp. 358-63. The method now used is a modification of Löwenthal's method, the cider being directly titrated with permanganate in the presence of indigo indicator. The permanganate is standardized by means of "pure tannin." All permanganate reducing substances are of course included. The method is only comparative. Gravimetric methods are not available, since it is not practicable to get a residue of constant weight by the evaporation of cider. Precipitation by potassium dichromate is not suitable, since gallic acid is also precipitated. Fleck and Sonnenschein have used copper precipitation methods, assuming that a constant relation exists between copper oxide and "pure tannin." This assumption is not warranted. The colorimetric method of Jean is misleading. Neubauer titrated with permanganate, then detannized with animal charcoal and then titrated again. His results are too high, since gallic acid and other non-tannins are absorbed by animal charcoal. Neubauer realized that his method could only give results in terms of the tannin used to standardize his permanganate solution. Trotman and Hackford (*Collegium,* 1906, p. 67) precipitate tannin with strychnine in dilute alcoholic solution, and weigh the precipitate, assuming tannin to be digallic acid. Nierenstein, Fischer and others have shown this assumption to be untenable. The method which the author regards as the best is to titrate with permanganate, then detannize by means of casein and again titrate with permanganate. The indicator used is a solution of indigo carmine in dilute sulphuric acid, about 5 grams per liter. The permanganate solution contains 1 gram per liter. About 10 cc. of the latter are required by 20 cc. of the indigo. To make a determination, 5 cc. of cider are added to 750 cc. of water in a porcelain dish, with 20 cc. of the indigo solution. The permanganate is run in slowly, with vigorous stirring. When the end-point is reached, the liquid is a clear golden yellow with a tinge of pink around the edge. To detannize, the solution is shaken 15 minutes with 1 gram of fat-free casein, filtered, shaken 15 minutes with a second gram of casein, and then filtered again. The permanganate solution used was tested against a number of samples of "pure tannin," and an average of the results employed in estimating the tannin content of the samples of cider. This value was, 1 cc. permanganate = 0.00543 g. tannin. The percentage of tannin found in the ciders tested ranged from 0.05 to 0.52.

An Analysis of the Saline Matter Adhering to the Flesh Side of Wet-salted East India Goat Skins. M. C. LAMB. *Collegium,* 1914, pp. 357-8. The skins in question are imported in barrels. The material analyzed was scraped off immediately after removal from the barrel, and gently ignited to destroy organic matter. The residue gave the following analysis: SiO_2 8.1 per cent., SO_4 48.6 per cent., Cl 9.9 per cent., Mg 2.5 per cent., Ca 2.2 per cent., Fe 1.8 per cent., Na 23.8 per cent., K 3 per cent. The moisture in the skins was about 20 per cent.

Digitized by Google

Celebration of the 25th Anniversary of the Foundation of the German Tanning School. *Collegium*, 1914, pp. 363-9. The celebration of the 25th anniversary of the Freiberg school took place from April 30 to May 2. Some 600 people were in attendance. A number of gifts to the school were announced.

Note on the Relation Between the "Feel" of Leather and Its Appearance Under the Microscope. R. FARADAY INNES. *J. S. C. I.*, June 15, Vol. 33, pp. 579-81. Sections averaging 0.17 mm. thick were made by hand with a razor from goatskins chrome tanned for glacé kid. Sections from mellow, well-feeling skins were easily spread out with needles on microscope slides. Those from hard "tinny" skins were hard to separate, the fibers being firmly cemented together. In the case of underlimed skins, the fibers are short and stuck together; stock properly limed, fibers long and well defined; stock overlimed, fibers long but ragged and fragile. Ten illustrations are given.

Proposed Combined International Congress of Leather Manufacturers and Chemists. *Leather Trades Rev.*, June 17, 1914. At the London conference of the I. A. L. T. C., two years ago, a proposition was made that the meetings of the Association should be held jointly with the International Leather Trade Congress. Correspondence between Dr. Stiasny, Hon. Secretary of the I. A. L. T. C., and Ettore Andreis, Hon. Secretary of the Congress, points to a probability that the two organizations will meet at Vienna in the last week of August. (See page 380.)

Relation of Acidity to Yield. An article on the above topic is presented by C. G. WILLIAMSON in the *Leather Trades' Year Book* under the title "$y = f(x)$." While a knowledge of the differential calculus may be general among British leather men, it is safe to say that an article on tannery practice would appeal more to American tanners and chemists if it avoided reference to such matters as dy/dx. Two diagrams are given, tending to show that the yield is higher with higher acidity, up to a certain point. The writer considers that the acidity should be such that the number of cc. of saturated lime water necessary to neutralize 10 cc. of filtered liquor is half as great as the number of barkometer degrees of the liquor. The diagrams cover a period of three years, and if they were sufficiently explained might be of real value.

Collodion in Leather Finishing. C. A. HIGGINS. *Leather Trades' Year Book.* Collodion gives a stronger film than linseed oil, shellac or resins. It is more easily applied than other finishing materials, and either as a pure varnish or as a vehicle for the application of pigments or other decorative materials, it is unequalled. The obviation of the liability to crack, which has been so great a drawback to patent leather, is perhaps the greatest of the many advantages offered by collodion finish.

Digitized by Google

Analysis of East India Tanned Goat and Sheep Leather. M. C. LAMB. *Leather Trades' Year Book*, pp. 198-200. These analyses were made at the instance of the Committee of the Federation of the Light Leather Trades.

Madras Tannages.

	Sheep			Goat		
	Prime Per cent.	City Per cent.	Fair Per cent.	Middle Per cent.	Ordinary Per cent.	City Per cent.
Leather fiber and insoluble	68.4	75.5	63.4	63.0	63.4	72.4
Fatty matter	10.2	4.7	18.3	15.6	18.3	9.7
Water soluble	10.0	7.2	7.7	10.0	7.9	6.7
Moisture	11.4	12.6	10.6	11.4	10.4	11.2
Ash and mineral matter contained in the above	0.6	0.6	1.0	0.8	0.8	0.8

Trichinopoly Tannages.

	Sheep			Goat
	A. Per cent.	C. Per cent.	B. Per cent.	Per cent.
Leather fiber and insoluble	70.2	69.8	68.7	74.5
Fatty matter	9.6	8.3	10.1	5.9
Water soluble	7.9	10.8	9.6	6.5
Moisture	12.3	11.1	11.6	13.1
Ash and mineral matter contained in the above	0.8	1.3	0.5	0.5

Dindigul Tannages.

	Sheep		Goat	
	E. Per cent.	F. Per cent.	G. Per cent.	H. Per cent.
Leather fiber and insoluble	71.5	73.1	73.9	77.0
Fatty matter	6.9	7.1	5.7	5.8
Water soluble	10.1	7.2	7.2	8.0
Moisture	11.5	12.6	13.2	9.2
Ash and mineral matter contained in the above	0.4	0.8	0.5	0.4

Miscellaneous.

	Sheep			Goat		
	Hyderabad S. Per cent.	Ambours T. Per cent.	Salem U. Per cent.	Vellore V. Per cent.	Coimbatore W. Per cent.	Ambours X. Per cent.
Leather fiber and insoluble	70.8	65.9	71.3	72.0	72.2	72.2
Fatty matter	7.8	13.3	5.4	10.0	7.1	10.4
Water soluble	10.7	10.1	10.8	6.1	8.5	5.6
Moisture	10.7	10.7	12.5	11.9	12.2	11.8
Ash and mineral matter contained in above	1.5	0.8	0.8	0.8	0.8	0.7

Digitized by Google

Up-Country Tannages.

	Sheep			Goat
	P. (oily) Per cent.	O. Per cent.	Q. Per cent.	R. Per cent.
Leather fiber and insoluble	66.6	60.8	65.1	66.5
Fatty matter	12.7	18.3	16.2	15.0
Water soluble	10.0	9.8	9.2	8.9
Moisture	10.7	11.1	9.5	9 6
Ash and mineral matter contained in the above	0.7	0.8	0.9	0.5

Power from Spent Tan. CHARLES E. PARKER. *Leather Trades' Year Book.* Several English tanneries are using producer gas plants to obtain fuel gas from their spent tan. The furnace used is larger than that used for coal. Before going into the producer, the spent tan is put through a press to expel excess moisture. The gas from spent tan has a high calorific value, especially that from myrobalans. Tar is deposited in the washer, from which salable products could probably be obtained if the quantity of tar were sufficient to warrant an installation.

The Measurement of Leather. G. A. SCHETTLER. *Leather Trades' Year Book.* This is a discussion of the faults of mea uring machines, with somewhat extended description (with illustrations) of a modern type of "pin-wheel" machine.

South American Slaughterings for Jerked Beef. *Consular Reports.* Since the beginning of the killing season, October 15, 1913, up to March 15, 1914, 237,000 head of cattle were slaughtered in the saladeros of Uruguay, Argentina and Rio Grande do Sul (the southernmost state of Brazil), a decrease of 53 per cent. from the corresponding period a year earlier, and of 70 per cent. from that two years earlier. This decline is due largely to the competition of the frigorificos, which pay higher prices than the saladeros can afford to pay for animals to be converted into jerked beef.

Government Supervision of Sewage Disposal Work. Luray, April 17.—H. B. Hommon, of the U. S. Public Health Service, has been at Luray for three weeks past preparing plans for the erection of a sewage disposal plant at the Deford tannery, the purpose of which is to purify the waste water arising from that plant.

Mr. Hommon went to Washington yesterday to complete arrangements there and the plant is to be erected this spring. When completed it will be the first of its kind in the United States and the model for similar plants to be erected by the other large tanneries of the United States.

The plant contemplated provides a process of tanks and filters by which the waste and filthy water will go through processes of purification.

Digitized by Google

Chemical, bacteriological and mechanical means are used to effect purification. The plant will be built on the rear of the tannery plant under the supervision of Mr. Hommon who will remain till its completion when another representative of the Health Service will come here to supervise its operation.

Being of an experimental kind the plant is installed entirely at the government expense.

Congress recently passed a law enabling the Bureau of Public Health Service to investigate unusual trade conditions in different parts of the United States. The manufacture of leather is one of the largest industries in the country and the waste from the tanning of leather produces unsightly conditions in water courses into which it is emptied and in some instances all forms of fish life are destroyed.

In many states legislation has been proposed looking forward to the prevention of nuisances arising from the presence of waste water in water courses. The government has undertaken to make a study of the waste coming from various manufacturing districts with the idea of assisting manufacturers to dispose of their waste water whenever laws are passed requiring that such waste shall be purified.

The tests being conducted at the Deford Co. plant are to serve as an example for all tanneries in this country using the same process of manufacture.

The nearness of the Luray plant to Washington and certain conveniences as regards construction of an experimental plant and its operation were the principal facts leading to selection of the Luray plant as the place for conducting the tests.

Determination of the Acidity of Leather. PAUL NICOLARDOT. *La Halle aux cuirs* (Partetechn.), 1914, pp. 65-9. Reference is first made to the paper of M. Jalade* which really has to do with sulphuric acid in leather rather than free sulphur. This is never found in tanned leather, and when originally present in chrome leather generally becomes oxidized later to acid. To determine free sulphur, the leather is extracted with chloroform. The sole official method for the determination of free sulphuric acid is that of Balland and Maljean with its various modifications but it has never been accepted in the laboratory of the technical section of the French artillery. The author agrees with M. Jalade in the necessity of fine division of the leather to secure uniform results, and a rotating plane has been used for this purpose 15 years in the artillery laboratory. Since 1903 the author has employed direct combustion with oxygen in a bomb for determining total sulphur. He differs only from M. Meunier in omitting the preliminary treatment with alkali.

The author has arrived at a method for the direct determination of free sulphuric acid alone without regard to the sulphur of the hide or neutral sulphates and also for determining the total acidity. To facilitate water extraction, the grease is first removed from the leather by chloro-

* Abstract, this J., p. 162, March, 1914.

Digitized by Google

form. The chloroform extract may be examined for total sulphur by the bomb process; it generally contains but traces of sulphuric acid or sulphates. The degreased leather is then boiled 3 hours with water. After filtration the acidity of the liquor is determined, spotting on litmus paper for the end-point. Free sulphuric acid and sulphates are determined by adding barium chloride. This test is controlled by another consisting in boiling the leather with the same volume of water for the same time in presence of barium carbonate. After filtration the acidity of the liquor is determined as before. A few drops of sulphuric acid are added to precipitate any barium passing into solution. After filtration, the filtrate is evaporated, ignited and tested for possible barium in a combination not precipitated by sulphuric acid (none was found).

The insoluble residue after filtration is taken up with boiling dilute hydrochloric acid and the insoluble part after calcination represents as barium sulphate the total sulphuric acid derived from the free acid and soluble sulphates. The following was obtained with a leather tanned three days in an acid liquor, all results being stated in percentage of H_2SO_4.

By the bomb, 3.5; total acid, Balland and Maljean, 2.53; fixed acid in ash, (B. & M.) 1.58; total acidity, boiling with H_2O, 1.96; acidity, boiling in presence of $BaCO_3$, 1.568; $BaSO_4$ in liquor after addition of H_2SO_4, 0.08; $BaSO_4$ in ash of boiled leather, 1.20.

Two leathers furnished to the service, in which about 1.2 per cent. free sulphuric acid was found, gave as follows:

	Balland and Maljean					
Bomb	Total	Fixed	Difference	Acidity H_2O extract	Acidity H_2O extract ($BaCO_3$)	$BaSO_4$ after HCl
2.8	1.93	0.67	1.26	3.18	1.715	1.38
2.15	1.50	0.39	1.11	2.45	1.22	1.28

In conclusion, the method of Balland and Maljean, even improved does not give certain results. The best procedure for total sulphur is combustion in oxygen in a large bomb at 10 atmospheres pressure. Total acidity of a leather may be determined with sufficient precision by boiling in presence of barium carbonate. In determining the acidity of the liquor, the total acidity is controlled. Magnesia may be used but the process is longer and less precise. W. J. K.

Meeting of the French Section, I. A. L. T. C. *Le Cuir*, June 15. The annual meeting of the French section was held May 29. Forty-six members were present, including Messrs. U. J. Thuau, President; J. Prevot, Vice-President; G. Abt, Secretary; A. Gagnard, Treasurer; R. Madru, J. Vaillant, L. Meunier, Ch. Monnet, P. Peltereaux, Jalade, and G. Jossier. The President announced that the next meeting of the International Association will be held in Vienna, August 24 to 29, 1914. L. Meunier presented a paper on quinones. G. Hugonin read a paper on chrome soaps, and U. J. Thuau one on sulphuric acid in leather and sulphited extracts. G. Abt spoke on the possible agency of microbes in the pro-

Digitized by Google

duction of salt stains, and L. Meunier on the chlorination of cod-liver oil. The viscosity of the oil is increased, and also its emulsifying power. A banquet was held in the evening. L. B.

Comparative Tanning Properties of Different Quinones. L. MEUNIER and A. SEYEWETZ. *Le Cuir*, June 15, 1914, pp. 465-9. The action of quinones on hide fiber is accompanied by oxidation, and the conversion of a part of the quinone to a hydroquinone. In discussing the properties of the various quinones, two points will be considered, their tanning power and speed of penetration. These may be observed much more satisfactorily on gelatine than on skin. The following substances were experimented on: 1, ordinary benzoquinone, $C_6H_4O_2$; 2, chloroquinone; 3, sulphonic quinone; 4, toluquinone, $CH_3.C_6H_3O_2$; 5, chlorosulphonic quinone A, (sodium salt) obtained by splitting monochlorhydroquinone; 6, chlorosulphonic quinone B, (sodium salt) obtained by splitting sulphonic quinone; 7, bromosulphonic quinone A, (sodium salt) obtained by splitting monobromhydroquinone; 8, bromosulphonic quinone B, (sodium salt) obtained by splitting sulphonic quinone. The experiment was conducted as follows: 5 grams of gelatine in thin leaves of uniform thickness was swelled for two hours in distilled water, then placed in a flask containing 200 cc. of recently boiled distilled water containing 0.2, 0.15, 0.1 or 0.05 gram of quinone. Each of these dilutions was used with each quinone, making a total of 32 flasks. They were stoppered and placed in the dark and examined after 18, 68, 96 and 120 hours. Quinone No. 1 required 120 hours to render the gelatine insoluble, in the highest dilution. None of the pieces were insoluble after 18 hours. Nos. 2 and 3 operated more rapidly. No. 4 did not render the gelatine insoluble after 120 hours with any of the dilution used, while Nos. 5 and 6 made it insoluble in 18 hours with all dilutions. Nos. 7 and 8, in all but the highest dilution, made the gelatine insoluble in 18 hours, and the highest dilution did not operate even after 120 hours. The penetrating power was tested in a separate experiment. That of 2, 3, 5, 6, 7 and 8 was very feeble, that of 1 somewhat greater, and that of 4 still greater.

L. B.

Chrome Soap in Chrome Leathers. G. HUGONIN. *Le Cuir*, June 15, 1914, pp. 469-71. In order to determine whether chrome soaps are formed when chrome leathers are fat-liquored with soaps, a chrome soap was made by treating a soap solution with neutral chromium chloride. The resulting chrome soap was insoluble in water, alcohol, ether or petroleum ether. It dissolved to the extent of 7 per cent. in benzine. Several samples of chrome leather which had been treated with soap were extracted with benzine in soxhlets, the solution evaporated and the ash of the residue found free from chrome. The author concludes that fat-liquoring of chrome leather with soap does not result in the formation of chrome soaps in the leather. L. B.

Digitized by Google

Sulphuric Acid in Leather and Sulphited Extracts. U. J. THUAU and R. MADRU. *Le Cuir*, June 15, pp. 471-9. The question of sulphuric acid in leather is of great interest to French tanners, many of whom have offered to the army leathers in the manufacture of which no sulphuric acid was used, only to have them rejected as containing too high a percentage of this acid. Many studies of this subject have been made, but the question is still far from being satisfactorily solved. There is general agreement that the method of Balland and Maljean is inexact because it transforms amorphous sulphur and that of sulphides, sulphites, bisulphites, of sulphates of volatile bases, and organic sulphur in general into sulphuric acid and estimates it as such. In a recent work, published in *Annales des Falsifications* (April, 1914), M. Nicolardot has described a method which at first glance appears satisfactory, since it should give both the total acidity and the free sulphuric acid. The authors next go to some length to disprove M. Nicolardot's assumptions as to the presence of free sulphur in leather. They suggest that the condemnation of the leathers referred to in the opening sentence is due to the presence of sulphur derived from various materials, and wrongly reported as sulphuric acid, and quote Dr. Dufour to the effect that sulphur derived from bisulphited quebracho has been the cause of such condemnation. The mixture of sulphited quebracho with oak or chestnut is liable to produce sulphurous acid, by the action of the organic acids of the oak or chestnut on the sulphites of the treated quebracho, and the oxidation of this sulphurous acid may then furnish free sulphuric acid to be taken up by the leather. Methods of estimating SO_2 in extracts are discussed. If the extract is diluted with water and boiled, the SO_2 present free or as bisulphite should distil over and may be caught in an alkaline solution and determined. The residue left in the flask may then be treated with H_2SO_4 and again distilled, expelling the SO_2 present as sulphites, which is caught in the same way. This method, however, is not dependable. The authors prefer to determine the total SO_2 by difference, first determining the sulphates in a sample of the extract, as usual with $BaCl_2$, then treating a similar sample with K_2CO_3 and KNO_3, thus converting all SO_2 into sulphates, and determining sulphates again. An examination of two bisulphited extracts by the distillation method showed that while the total SO_2 present as shown by the gravimetric method was the same, the extract bisulphited under pressure gave up less SO_2 on boiling than that bisulphited in the open. The authors suggest that this indicates a more stable combination between the sulphur and the tannin in the case of the former, and they therefore believe the extract bisulphited under pressure to be preferable to the other. L. B.

Simultaneous Meetings of I. A. L. T. C. and International Association of Leather Manufacturers. Since the note on page 374 was in type, the July *Collegium* has come to hand with preliminary program of the Vienna Conference of the I. A. L. T. C., August 24-29, and a notice that the

Digitized by Google

meeting of the International Association of Leather Manufacturers will be held at the same time and place. A few joint sessions will be held for the discussion of subjects of common interest.

The Salting of Hides and the Avoidance of So-called Salt-Stains. C. ROMANA and G. BALDRACCO. *Collegium*, July, 1914, pp. 517-19. In order to test the suggestion of M. Tainturier in regard to the effect of washing hides before salting, a number of fresh hides were obtained from the abattoir. After careful washing in running water, they were drummed for half an hour in running water and horsed up (hair out) over night. The hides were divided into six lots, one salted with denatured salt alone, 15 per cent. by weight, and for each of the others 1 per cent. of another substance was added to the 15 per cent. of denatured salt; sodium fluoride, borax, sulphate of soda, carbonate of potash, or chloride of potash. They were then piled for 24 hours, after which they were folded in the usual manner and laid away for 15 days. Careful examination showed that the hides were perfectly preserved. They were then limed, the limes being sharpened with sulphide of soda, and then unhaired and fleshed. All six of the lots were free from stains, the grain being white. Those to which borax had been added were especially fine, and the fluoride of soda lot still finer, the grain being very fine, white and supple. The authors conclude that thorough washing is a valuable aid in preventing salt stains, and that sodium fluoride added to the salt improves the product. L. B.

PATENTS.

Fleshing Machine. British Patent 3,763. A. H. KEHRHAHN, Frankfurt, a. M., Germany.

Leather Oiling Machine. British Patent 3,730. G. V. ANDERSON, Philadelphia, Pa.

Leather Staking Machine. British Patent 2,442. W. F. FINCH, Liverpool.

Leather Staking Machine. British Patent 5,333. MOENUS MACHINE COMPANY, Frankfurt, a. M., Germany.

Tanning Extract. British Patent 5,369. X. F. DEBEDAT, Bordeaux, France. The rasped wood of heather (*erica scoparia*) is treated with water at about 60° C. and evaporated in a vacuum, making a practically colorless extract.

Buffing Machine. British Patent 6,013. M. H. SMITH, London.

Water-proofing Leather. British Patent 29,997. K. HARTMANN, Berlin.

Process for Making Water-proof Leather. British Patent 4,488. J. HERBERT, London.

Digitized by Google

Artificial Zeolites for Softening Water. British Patent 5,783. P. DE BRÜNN, Dusseldorf, Germany. Solutions of alkali aluminate and alkali silicate, together with sodium sulphate or chloride, are mixed and boiled. The bulky precipitate is washed, calcined and dried.

Method of Subjecting Lacquered Leather to the Light Treatment. U. S. Patent 1,099,378. A. JUNGHANS, Schramberg, Germany. The leather is exposed to light rich in ultra-violet rays, the formation of ozone being prevented.

Process of Making Formaldehyde. U. S. Patent 1,100,076. H. VON HOCHSTETTER, Constance, Germany. A mixture of air and methyl alcohol is sprayed over a catalyst.

Process of Making Tanning Extracts. U. S. Patent 1,098,348. The raw material is subjected to dry heat before leaching, to prevent bacterial action.

Method of Storing Hides. U. S. Patent 1,098,005. WILLIAM H. ALLEN, Detroit, Mich. Tanned hides are kept in condition for dyeing by being stored in a room whose atmosphere contains a little formaldehyde and is saturated with moisture.

Oiling-off Machine. U. S. Patent 1,101,762. CHARLES E. SLOCOMB, Wilmington, Del.

Leather Staking Machine. U. S. Patent 1,101,763. FRANK F. SLOCOMB, Wilmington, Del.

Leather Finishing Machine. U. S. Patent 1,102,368. WILLIAM B. TURNER, Wilmington, Del.

Bark Rossing Machine. U. S. Patent 1,102,657. WILLIAM G. HAFNER, Clay, N. Y.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. IX SEPTEMBER, 1914 No. 9

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1914, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VEITCH, } . . . Past Presidents

OFFICERS, 1913-'14

PRESIDENT—W. K. ALSOP, Ridgway, Pa.

VICE-PRESIDENT—C. W. NORRIS, 80 South Street, New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

LLOYD BALDERSTON, Ridgway, Pa.

C. R. OBERFELL, Harrisonburg, Va.

T. A. FAUST, 323 Academy Street, Newark, N. J.

ELECTIONS.

ACTIVE

R. H. W. Lord, Gotham, Mass.

Leo. A. Mantner, % B. D. Eisendrath Tanning Co., Racine, Wis.

Ralph E. Porter, % St. Paul Tannery, So. St. Paul, Minn.

Dr. Theodor Veit, % New York Quebracho Extract Co., Inc., Greenpoint, Brooklyn, N. Y.

ASSOCIATE.

Clarence M. Allen, % New York Quebracho Extract Co., Inc., 17 Battery Place, New York, N. Y.

A. R. Andreae, 122 Hudson St., New York, N. Y.

Walter P. Nichols, % C. A. Spencer & Son Co., 183 Essex St., Boston, Mass.

Otto Haas, 40 N. Front St., Philadelphia, Pa.

Digitized by Google

CHANGES OF ADDRESS.

G. Gifford Eysenbach, to 84 N. Lansdowne Ave., Lansdowne, Pa.

H. S. Frederick, to 413 Newhall St., Milwaukee, Wis.

Paul Hayes, to 8 Browning Ave., Dorchester, Mass.

A. H. Lockwood, to 166 Essex St., Boston, Mass.

COUNCIL MEETING.

A meeting of the Council of the American Leather Chemists Association was held at the Chemist' Club, New York City, on Monday afternoon, August 3rd at 2 o'clock.

There were present, Messrs. Alsop, Norris, Reed, Hoppenstedt, Balderston, Oberfell and Faust.

W. K. Alsop presided, H. C. Reed, Secretary.

Minutes of the last meeting were read and approved

The secretary reported the payment to Dr. Parker, treasurer of the Procter Laboratory Fund, of $1,050.00, made up as follows: $730.00 from the A. L. C. A. and $320.00 from the National Association of Tanners.

Mr. Reed submitted a tentative report on the matter of S. & S. Filter Papers, stating that the ones sent him for examination proved very good and that the makers had promised to have better papers in the future. Some reported papers very good at present, others not so good. It was the consensus of opinion that all members of the Association should lay in a supply of S. & S. filter papers if they could, as in the event of a prolonged European war it might mean a shortage of the papers in question. The Council recommended in the event of such a happening, that Swedish No. 1 F filter papers be used in place of the S. & S.

The tentative program for the Annual Meeting, which will be held at Chicago, on Wednesday, Thursday, Friday and Saturday, October 28th, 29th, 30th and 31st, 1914, as submitted by Mr. Cudworth Beye, was approved by the Council.

The proposed change in methods was not approved. The reason for rejecting the change, was that the Council was of the opinion that if adopted it would be no improvement to the methods, but would further tend to complicate them.

The secretary was instructed to write to the chairmen of all

Digitized by Google

committees (where chairmen were appointed), as to the work they had done, or expected to do, on their various committees.

Names for membership were acted upon as shown above.

Nominations for officers for the ensuing year were made.

The headquarters for the annual meeting will be at the Hotel LaSalle, Chicago. The committees in connection with it were appointed as follows: Committee of Arrangements, Cudworth Beye, chairman, Dr. L. E. Levi and R. C. Jacobsen. Committee on the getting of papers for the meeting, H. C. Reed, chairman, with all the members of the Council, in addition to L. T. Roenitz, V. A. Wallin, C. M. Morrison, F. A. Loveland. The chairman was instructed to send out return postals to all members of the Association as was done last year.

The Council was of the opinion that the matter of holding the annual meeting in the spring should be brought up at the October meeting.

ANNUAL MEETING.

Tentative program for the eleventh annual meeting of the American Leather Chemists Association, in conjunction with the annual meeting of The National Association of Tanners, at the Hotel LaSalle, Chicago, Ill., Wednesday, Thursday, Friday and Saturday, October 28th, 29th, 30th and 31st, 1914.

Wednesday:	A. M.	A. L. C. A. 9.00.
		President's Address.
		Secretary-Treasurer's Report.
		Committee Reports.
	P. M.	A. L. C. A. Papers.
		Discussion.
Thursday:	A. M.	A. L. C. A. Papers.
		Discussion.
	Noon.	Luncheon.
		Round Table Discussions.
	P. M.	A. L. C. A. Papers.
		Discussion.
	6.30 P. M.	Executive Committee T. N. A. T.
		(Group meetings also to be scheduled.)

Digitized by Google

Friday:	A. M.	General Meeting T. N. A. T.
		A. L. C. A. Papers.
		Discussion.
	Noon.	Lunch, Allied Trades.
	P. M.	Joint Meeting.
		Discussion Tanning School, etc.
	6.30 P. M.	Complimentary to A. L. C. A. and Theater.
Saturday:	A. M.	A. L. C. A.
		Executive Session.

H. C. REED,
Secretary.

IGNAZ EITNER.

The number of *Gerber* for July, 15, is a single sheet containing the announcement of the death of an honored veteran in the field of scientific investigation of leather problems. Wihelm and Ignaz Eitner were associated in beginning the publication of *Gerber* forty years ago, and the news of the death of the latter in his eighty-second year carried sorrow to the large circle of readers of that highly valued journal.

Close upon this announcement followed the news of the great European war, which renders impossible the Vienna Congress of the I. A. L. T. C. and brings the keenest grief not only to Europeans but to us of America who have so many good friends in all the contending nations.

THE VALUE OF SCIENTIFIC TRAINING TO THE LEATHER MANUFACTURER.*

By Prof. E. Stiasny, Ph. D.

Much has been said and published to convince the practical man of the value of science in industrial enterprises. One is, however, scarcely justified in believing that the great majority of leather manufacturers are fully convinced of this value, at least so far as the higher kind of scientific research goes.

The advantages of having tanning extracts and other materials

* *Leather Trades' Year Book*, pp. 95-99.

Digitized by Google

tested by a chemist are widely acknowledged, and the trade can scarcely do without such chemists' help in these days. It is even more and more understood that a good chemist with practical abilities and considerable experience is a very useful man in a tannery, as he will introduce chemical control in the works, and probably find many instances where money can be saved, or where the present methods can be improved and the value of the finished article increased. The number of young chemists entering leather works every year shows distinctly a growing appreciation of this method of applying science.

There are, however, other possibilities of making use of science, less obvious perhaps than those mentioned above, but surely not less important. These possibilities are based upon scientific research, the results of which may not be of immediate practical value, but are of far-reaching importance, and throw valuable light upon the obscurity which still surrounds many of our technical processes, and the chemical nature of the materials used in leather manufacture.

It would seem at first sight that it is largely a matter of chance for results of practical importance to follow from researches conducted for purely scientific purposes, and that the yield of such valuable results may be rather small compared with the amount of work done. This view is not necessarily true; the benefit derived from such research can be distinctly increased by a systematic organization of the education of those who have to apply theoretical results to practical ends. It is indeed mainly an educational question, viz.:—firstly to create the spirit of research in the mind of the student who chooses this branch of applied chemistry, and secondly, to give the student such training as will enable him to see the practical possibilities in the results of research work carried out by himself or by others on purely theoretical lines. The number of useful suggestions which can be obtained in this way is quite extraordinary, and they will certainly repay for the time and labor spent on the necessary training, and for the further expenditure of about one hour daily in consulting journals of pure and applied science.

The following example, familiar to every leather trades chemist, may be chosen to illustrate and support the above state-

Digitized by Google

ment:—In the fifties of last century F. Knapp published his famous papers on the theory of tanning and on mineral tannages, in which he actually describes the one bath chrome tannage almost in the same way as it is carried out to-day. But practical tanners in those times did not trouble about chemistry, and nobody took any notice of Knapp's researches.

Had there been one chemically trained tanner who had taken the trouble to repeat Knapp's experiments, and to work out Knapp's suggestions on a practical scale, surely this man would have been recognized as the pioneer of practical chrome tannage. However, there was no such tanner, Knapp's invention was forgotten, and only revived after Schultz's invention of the two bath chrome tannage.

Was it really necessary—this question must be asked—that so many years should pass before Knapp's invention was developed into a practical success? What was the reason for this slow progress, and how can things be improved in future? Well, the reason for the slow development of technical methods in leather industries lies in the fact that those who were engaged in the practice of leather manufacture were not in touch with that other world where science is taught and cultivated. They did not know of Knapp's researches, they did not care for his discoveries, nor did they appreciate the value of his endeavors to understand the principles which underly the processes of leather making.

This was the state of affairs a few decades ago, but no doubt things have improved since; it, in fact, is very improbable at the present day that a discovery of the type of Knapp's could remain unknown and untested during such a long period of time. Yet even now confidence in the value of research is not as strong and as general as it ought to be in industrial circles, and the following little story is characteristic of the feeling which still prevails in the minds of some practical leather men. It is but a few weeks since a student of the Leeds University Leather Industries Department tried to find an opportunity of spending his Easter vacation in some light leather works. Needless to say, he did not succeed—I did not anticipate for a moment that he would—but on three occasions, in conversation with the head of

Digitized by Google

a firm or its manager, the question was put to him, "Why on earth did you choose the Leeds University if you wanted to learn something useful in connection with leather manufacture?" This question was followed by a few skeptical remarks on the value of higher education, and the student was told ironically that he would be welcome to their works if he would show them how to finish their special product at a saving of a few pence upon the cost of the process they were already employing; but they supposed that such a useful question was not likely to be dealt with at the university!

From these remarks it seems that some practical tanners have even now a very imperfect idea of the scope of technical education in an institution of a university type.

A student who comes to the Leeds University, or to any other institution of similar educational aim and standing must not expect to get better information on merely practical questions than he could get in a tannery or finishing shop. The university training is intended to provide the student with sufficient knowledge of chemistry, physics, bacteriology, etc., to enable him to understand and apply the scientific principles on which the processes of leather making are based. It aims at opening the student's mind so that he can look upon all the processes not merely from the practical man's point of view, but with the eye of the scientist, who thinks in a language and arrives at conclusions which the merely practically trained man can hardly use or reach. The student, moreover, must not only learn the different methods as they are in use at the present time, but his mind must be trained to search for improved methods and for new processes. He must learn to keep in contact with the literature of pure and applied chemistry, and must be trained to apply quickly to his own branch of applied science what he finds in the different books and journals. Finally, he must learn to do research independently, both on practical and theoretical lines, so that he can study questions of immediate importance to his work and also carry out experiments for future development. Take a man with such a training, and of course with natural abilities, and compare him with an intelligent man of the old practical type, and you will find the former to possess far greater

Digitized by Google

possibilities and to be of far greater value to the works, provided of course, that he is used in the right way, and not merely engaged on such kinds of work as a man without his training would be able to do. In fact, there is more money in scientific training and in scientific research, than many a tanner believes.

To come back to the above example, my student after learning that his chemical knowledge was not supposed to be of any practical use to himself or to his employer, went to the docks to look at the great quantities of raw skins which are piled there and open for inspection. There he saw a number of bales of tanned sheepskins which, although of excellent quality were offered at half their usual price, the only reason being that they were badly spotted with dark stains. My student obtained a small sample and coming back to the laboratory soon discovered the nature of the spots and an easy method of removing them. He wrote to London at once and had the bales bought by a friend who, I am sure, will appreciate now if he did not before, that chemical training can be of direct practical value. How many more instances of a similar kind are wanted to convince the practical leather man, and how far are we from the time when even the value of higher scientific research will be appreciated?

SOME REMARKS ON LIMING.*

By J. T. Wood.

It may be, I think, safely stated that the liming problem has only received the attention it deserves in quite recent times—one might say since 1900. Previous to that date, chemists and others connected with the tanning industry, especially the International Association of Leather Trades Chemists, had devoted their attention to perfecting methods for the analysis of tanning materials. In 1909, at the suggestion of Mr. Seymour-Jones, this Association turned its attention in part to the problems connected with the raw skin, and appointed an International Commission for the preservation, cure, and disinfection of hides and skins.

* *Leather Trades' Year Book*, pp. 152-5.

Digitized by Google

Such matters are of vastly greater financial importance to the tanner than small differences in the analysis of tanning materials, since, if he does not get good raw material, he cannot make good leather.

At the Paris Conference of the I. A. L. T. C. in 1910, Dr. Gordon Parker and the author were appointed to consider and recommend standard methods for the control of limes, and the checking of loss of hide substance during the initial processes.[1] Certain recommendations were laid before the London Conference in 1912,[2] and provisional methods adopted. It is hoped that this beginning may lead to as good results as have been attained in the case of the analysis of tanning materials.

In reply to the question of Mr. Seymour-Jones in a recent article[3] "Why do we lime a hide or skin?" Professor Procter points out that primarily we lime a hide to remove hair and epidermis structures, but produce at the same time other effects, some of which are useful, but which *might be produced in other ways*.

As to what are the useful effects, would take too long to go into in the space of a short article, but most tanners are acquainted with the detrimental effects of lime, and the necessity of removing it more or less completely prior to the tanning processes proper.

The author in his book on the "Puering and Bating of Skins"[4] has discussed the question whether a skin which had never been submitted to the tanning operation could be bated by enzymes alone without the addition of other compounds in the bate, which are essential to the proper bating or puering of limed skins. Enzymes (of which trypsin, the digestive enzyme of the pancreatic juice, may be taken as an example), dissolve the interfibrillary substance, and thus separate the fibre bundles into their finer constituent fibrils. This is precisely one of the useful actions performed by lime, so that if we could unhair and bate a skin without the use of lime, the dissolving effect due to it

[1] *Collegium*, 1910, p. 418.
[2] *Collegium*, 1912, p. 121; 1913. p. 73.
[3] *Collegium*, 1913. p. 14.
[4] p. 130.

Digitized by Google

could be produced in the bates where it can be more effectively watched. Quite recently Dr. Otto Röhm of Darmstadt, has attempted to solve the problem by the use of an enzyme preparation whereby the skin is unhaired and bated at one operation.[5] If this is successful in practice, the preparation of skins for tanning will be greatly simplified. Since no alkali would be introduced into the skin, all the various processes for getting rid of it, would be done away with, and the preliminary operations could be conducted antiseptically.

But there is another useful effect which lime may have. Payne, in a communication to the author some years ago, considers that the addition of calcium to the hide fiber is necessary for the proper formation of leather, at any rate, for vegetable and oil tannages. He considers that a true chemical combination of lime and the hide fiber takes place.

It seems highly probable that this view is correct, since the foundation stones, so to speak of hide, are amino-acids (that is, ammonia (NH_3) in which one hydrogen atom has been replaced by an acid radicle), and such bodies can combine with alkalies like lime, to form salts, and such salts may combine in different ways with different tanning materials.

In addition to these effects there is the swelling action of lime. This has hitherto been explained by somewhat complicated theories, which place skin substance and gelatin in a different category (colloids), and subject to different laws to those which govern ordinary chemical reaction. The recently published papers of Professor Procter[6] on the acid swelling of gelatin, throw an immense light on this question, and his discoveries are of far-reaching importance, not only to tanning chemists, but also to physiologists. These discoveries are, I must confess, difficult to explain in a simple way, but put briefly, the chief point is that gelatin, under certain conditions, can form salts with various acids, which are stable or in equilibrium with the same acid in the outer solution. These salts split up (or ionize) to their constituent molecules in the acid solution in the same way as common salt ionizes in solution, and is thus able to con-

[5] *Collegium*, 1913, p. 374.

[6] *Transactions Chemical Society*, 1914, p. 313. This J., May, 1914.

Digitized by Google

duct an electric current. These free wandering molecules, or ions, as Faraday called them, endeavor to escape into the outer solution, but since the gelatin molecule is solid, and cannot move water from the solution enters the system, and produces a pressure, which is the cause of the swelling.

Although the case of swelling by lime is different to that of swelling by acids, there seems no reason to doubt, in the light of Professor Procter's discovery, that in this case also a salt of gelatin or collagen is formed, since gelatin contains both basic and acid groups, and can therefore fix both alkalies and acids. In the case of lime therefore the gelatin must function as an acid, and form, what we might call, a "gelatinat" of lime.

As we have seen, lime dissolves the interfibrillary substance of the skin. This substance is nitrogenous, and enables the solution to support the life of bacteria. These develop in the liquor, and secrete enzymes, which dissolve not only the interfibrillary or cement substance, but also attack the skin fiber itself, and valuable substance is lost, which should be made into leather. Consequently an old lime is very detrimental, and especially so in fellmongers' yards where the pelts are put into a gathering lime prior to being sent away to the tanner. In one case which came to my knowledge, the fellmonger could not remember ever having cleaned out the limes, but had strengthened them from time to time. These limes contained over 3 per cent. of dissolved skin, an amount equal to a good pelt, weighing 7 lbs. in every two buckets of the liquor. The alkalinity was nearly three times that of a freshly made lime liquor. These gathering limes ought to be cleaned out, and made up fresh at least once a month.

Since the use of sodium sulphide and other depilatories has become general, there is a further danger in the use of old limes. Some fellmongers put the sulphide pelts, after pulling, through an old lime pit; the sulphide accumulates from lot to lot until the liquid is actually strong enough to paint with. The pelts should be washed for half-an-hour in clean water *immediately* after pulling, and then transferred to a moderately good lime, and given an occasional draw until ready for the leather dresser.

In conclusion, it is the duty of all of us who are connected

Digitized by Google

with the leather trade to strive for perfection in our methods of working, so as to produce beautiful leather. No one will deny that there is a dearth of such leather at the present time; prime best skins are difficult to procure, and fetch good prices, so that the fellmonger would be bound to reap a substantial reward for his trouble.

A COMPACT KJELDAHL APPARATUS.*

Hugh Gœrner Bennett, M. Sc., F. C. S.

An immense number of forms have been suggested for the apparatus used for the distillation of ammonia in Kjeldahl's method for estimating nitrogen. The particular arrangement here suggested has been used by the writer for some years and found exceedingly suitable on account of its compactness and convenience. The receipt of several private enquiries as to its exact arrangement has encouraged the writer to give it a wider publicity.

The boiling is conducted in a one litre Jena conical flask. A flask of this capacity allows of a greater dilution than usual of the liquor to be boiled, which dilution (with the usual help of a little granulated zinc) entirely obviates the objectionable bumping of the stronger caustic soda solutions. It has the further advantage of giving more margin for the "frothing" which inevitably takes place in the estimation of ammonia in lime liquors by the distillation method. Lime liquors, moreover (whether in estimating free ammonia or total nitrogen), are even more liable to "bump" than caustic soda solutions, so that this rather large flask is perhaps particularly an advantage to the leather chemist.

The usual tap funnel for delivering the caustic soda solution is dispensed with, as this is not only an unnecessary encumbrance but also a fertile source of error. A tap funnel is never very convenient to fit through a bung which contains also another fairly wide tube, and its use only involves more apparatus to wash. Strong caustic soda solution is a somewhat unpleasant reagent to store and handle, and nearly always causes trouble

* *Collegium*, 1914, pp. 482-4.

Digitized by Google

with taps and stoppers. The writer has made a practice of quickly weighing out the caustic soda in the "stick" and adding it directly to the distilling flask immediately before the distillation is commenced. No loss of ammonia is possible if the flask be immediately connected up, for the liquor in the flask has not only to dissolve the caustic soda but also to have its excess of sulphuric acid neutralized before any evolution of ammonia can take place. The dilution also prevents a too sudden evolution of ammonia.

A spray trap is first connected to the distillation flask, and is a very convenient way of preventing any caustic soda solution from being carried over to the receiver. This also contributes materially to the compactness of the apparatus by avoiding the tall reflux condensing tube usually employed for this purpose.

The spray trap is connected with an all-glass, double-acting condenser, which is fixed vertically (see Fig. 1). It is this condenser which is the chief cause of the compactness of the apparatus. Its length is only 12 inches, and its condensing efficiency is said to be equal to that of an ordinary Liebig's condenser of four times that length.[1]) Being all glass there are no rubber connections or stoppers to get out of order, a considerable advantage over many double-acting condensers.

According to Sutton (Volumetric Analysis, p. 85, 10th Ed.) there is no need whatever for the condenser to have a continuation which dips right into the acid in the receiving flask, still less need for this flask to be fitted with a bung and trap, as is often seen. Cold water has a very strong affinity for ammonia and unless the temperature of the laboratory is very high there is no danger of loss of ammonia. This suggestion not only simplifies the apparatus, but also makes it much more convenient to remove and replace the receiving flask. As there is no fitting to be done one flask is as good as another as receiver. Three hundred cubic centimeters Jena conical flasks are preferred by the writer.

This open receiver has been recommended by several experimenters, sometimes working only with an air condenser! The

[1] This condenser is supplied by Messrs. E. B. Atkinson & Co., 24 Dock Street, Hull.

Digitized by Google

writer, however, chose a double-acting condenser for the express purpose of ensuring a low temperature for the distillate, in order to make more certain that no ammonia is lost. Experiments have also been made with known weights of pure dry ammonium chloride, and the theoretical result has been obtained in

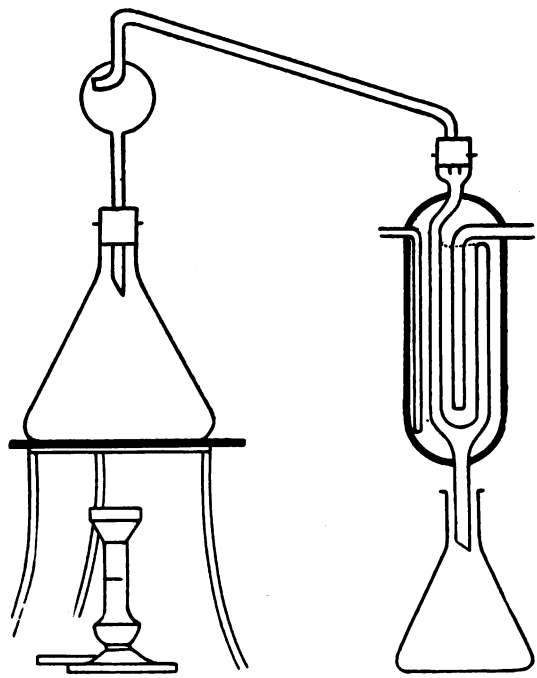


Fig 1

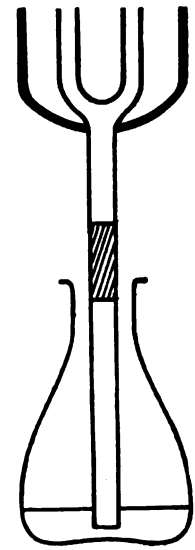


Fig. 2

successive experiments. Duplicate estimations of hide-substance in leather have also not only agreed but also have given the same result as in a further experiment in which a leading tube was used which dipped right into the acid. There seems little doubt that with an efficient condenser an open receiver is quite safe, but those who are at all nervous on the point, can easily connect the condenser end to a short glass tube, and by raising

Digitized by Google

the receiver with a wooden block cause this tube to dip into the acid (see Fig. 2).

The whole apparatus as here described is only about 22 inches high, and if set up close to a tap and sink, occupies only about 18 inches of the bench frontage—a consideration in many laboratories. The apparatus is so compact indeed that the receiving side is very near to the distilling side, but by interposing vertically between these parts a piece of asbestos millboard, any radiation of heat to the receiver is effectually prevented.

The writer has found N/5 hydrochloric acid and N/5 caustic soda the most convenient reagents. Decinormal acid gives an amount of liquid too large for convenient titration, on account of the increase due to the distillation. Methyl red (with caustic soda) as indicator is a great improvement on methyl orange, carminic acid or any other indicator yet suggested for this work.

THE PROSPECTS OF LEATHER MANUFACTURE IN CHINA.*

By J. Dyson Withinshaw.

China and her troubles have occupied quite a prominent place in our newspapers during the last few years; her "trade possibilities" and "abounding natural resources" have been expatiated upon *ad nauseum;* but whether all that has been written has induced any British capitalist to consider China as a possible site for modern tanneries, I do not know.

We are assured, and truly, that China is in a state of unrest, that "White Wolf" is plundering and laying waste in the north. Such a state of affairs in a European country would seem the end of all things and would embroil the whole population. In China this condition of semi-impotent government has obtained for so long a time as to become the normal. Only an infinitesimal percentage of the population are concerned in these various rebellions; the great bulk of the people pursue their ordinary avocations with a long-suffering industry, only to be achieved by a Chinaman.

* *Leather Trades' Year Book*, pp. 112-18.

Digitized by Google

When a part of one of the rivers (these are the trade routes, there are no roads), leading to Canton is held by "pirates," the native merchants are not unduly troubled, they pay a sort of tribute on each bale of silk, leather, or whatever they wish to pass through that part of the river. In any case the officials of that route would have required some payment, and these "pirates" are smart enough to avoid killing the goose that lays eggs for them.

There seems little prospect of anything but unsettled political conditions in China for some time to come, and it is with prospects under these conditions that one must deal. The great trade boom which will undoubtedly arrive when China achieves stable and incorrupt government, is, in the writer's opinion, not likely to benefit the present generation of leather men.

The amount of leather imported into Hong Kong is increasing, but the writer's opinion is that no great amount of trade in sole or upper leather can be done with China; practically it means paying freights to Europe or Australia and back, to use very dear labor in the manufacture, and materials which cost at least as much in Europe as in China. It also means a whole host of intermediate profits between the butcher and the Chinese leather merchant.

A friend in Hong Kong who is one of the largest importers of leather at that port, told me that leather gives them more trouble than anything else they handle. He showed me a lot of chrome (for uppers) which was ordered on sample by a native merchant. It was fully up to sample, but had been refused; in fact the Chinese merchant would not even make an offer for it. The sample was black flesh and grain, but the bulk was not so deeply colored on the flesh side. My friend said "This Chinaman is scrupulously honest and is incapable of a crooked deal, but how on earth can I explain this to the senders of this leather?" At the same time he showed me a delivery of sole leather sent to sample by a north of England firm. This lot I thought better than sample, but because it was not exactly the same color, this had also been refused. It was always my experience that the local buyers were much more exigent about the appearance than the quality of goods.

Digitized by Google

It is obvious that any British firm who started their own branch out in China and had competent leather men at that end, would monopolize what import trade is to be done. It is, in fact, somewhat surprising that this has not been done. However, their business would only last until, as must happen in the near future, local hides are tanned by modern methods on the spot.

The leather trade in China undoubtedly offers a very wide and promising opening for European enterprise, and one hopes that British tanners may be first in the field. At Haiphong, in French Indo-China, a large tannery has been running for about two years. It is a French company employing three French experts. They make sole, belting, and patent leather. This last is in great demand among the Annamites, but there is no demand for it in China proper. The Haiphong Company are doing extremely well and have been extending their premises continuously to meet the local demands for their leather.

There is also in Shanghai a very small tannery which has had a chequered career, it was idle for some time, but, I understand, is about to be started again.

The Canton tannery which the writer built for the government in 1910, was closed by Yuan Shi Kai's officials when the so-called second revolution, led by Chinese, who have been educated in foreign universities, was crushed at the end of last year. This is a large well-equipped yard, with pits and drums capable of turning out about 1,500 hides weekly.

The Japanese are credited with having greatly improved their leather. If the leather they send to China is a fair sample of their attainments, their production must have been pretty bad originally.

There is an enormous quantity of sole leather used in South China; much is imported from Singapore, but the bulk is made in small tanneries all over the country, by the most antiquated methods imaginable. Usually a man and one or more of his sons do the whole work, turning out perhaps half-a-dozen hides weekly. They use various tanning materials grown locally. I do not know the English names for any of them, but tested several, they came out at least double the price of our extracts, etc. Myrobalans are grown there, and I saw many samples, they

Digitized by Google

were small but of excellent color and weight, but the price was prohibitive. Sole leather of good quality can be made out there and sold at a price to compete with this local rubbish. There is also a fair demand for leather belting and hydraulic leather.

They make a very cheap upper leather with which our leather could not compete, it is very poor but much better than their sole, and satisfies the local buyer. Hides for this upper leather are split by hand and then smoked; they are quite a good color, stain easily, but are rather tinny.

On my arrival in Canton I saw some tons of these split hides lying on a wharf and was very puzzled to know what they were, all I could be sure of was that they were some kind of leather outside my experience, and that they had been through a splitting machine. When my interpreter told me they were split locally by hand, that the workman used "one small knife, all the same any other knife," adding the statement that they could split one hide into ten layers—I remember wondering uneasily whether he was telling me such unnecessary lies, because I looked as much a tenderfoot as I felt! Since then I have seen so much of this hand-splitting, at my own and other yards, that it seems a very ordinary occupation. At a small native tannery I once saw a water-buffalo hide split into thirteen layers. These thin flesh splits are smoked and then used to cover wooden boxes, etc.

There is an abundant supply of hides at Canton and ports up the Canton River; one dealer offered me 4,000 monthly, and there were two other collectors in the same river-side town. I did not tan any pig-skins, but the officials caused enquiries to be made, and told me that large numbers were available in the interior, some hundreds of miles up the river.

The average Chinese coolie is a most excellent workman and a very likeable fellow, having a large share of that most desirable possession, a sense of humor. If one has the knack of handling Chinese workmen, they are very easily trained as curriers, fleshers, etc. The coolies, though such willing workers that they really seem to come somewhere near Kipling's ideal, who will work "for the joy of the working," are very "kittle cattle" to handle. They will only work willingly so long as they are convinced that

Digitized by Google

their toil is accomplishing something, and that the method they are using is the best for the purpose. I found that it was quite impossible to get them to haul up a lime or handler for the purpose of pulling it back into the same pit and liquor. One could, of course, have dragooned them into doing it, but this method is out of the question when dealing with Chinese. After most careful conning of this question I gave the various foremen a quantity of harmless solution, telling them to add half-a-pint at each handling. For the limes I gave them an arsenic solution, impressing on the foreman, in case he doubted the stuff, that he must not taste it as it would "makee dead." No doubt he tried its effect on some unfortunate animal,—anyway we had no further trouble as to the handling.

The difficulties incident to tanning in the tropics are by no means insuperable; though finishing is quite an interesting operation when, with a temperature of about 100° Fahr., the atmosphere is so damp that goods exposed to it for 24 hours would be pronounced nicely sammed for shaving by a currier. During the hottest months one's water supply is about 90° Fahr.

Few tanners, I should imagine, have had to dig for quebracho extract. Twenty tons of this material—solid and packed in small bags in the ordinary way—arrived before we had finished building. It was stored in a detached hide warehouse which was finished. Some months later one of the men informed me "that black stuff plenty makee walkee." The damp and heat had melted the whole lot, it was a solid sticky mass, the 6-inch drain pipes were full of it, and we had to dig them up to recover it.

The manager of a tannery in China will need a very large share of tact; the power to retain an unruffled countenance, with a temper perfectly under control and a courteous demeanor; under all circumstances. The Chinese have this power, and they do not understand, or respect, a foreigner who lacks it. Unjust treatment of a workman or customer might result in the stoppage of any factory in China, so great is their power to boycott. A complaint would be laid before the local "Merchants' Guild," who, if they think such complaint justified, will endeavor to obtain satisfaction from the offending firm; should this firm fail to act in what they (the Merchants' Guild) think a just and

Digitized by Google

reasonable manner, a boycott will be instituted which will certainly prove fatal. Several cases of trouble with the "Canton Merchants' Guild" came to my notice while I was out there, and I must say that their decisions always seemed eminently reasonable. To understand how thorough a boycott may be, one has only to remember that during the boycott of the Japanese a few years ago, the people not only refused to buy Japanese goods, but publicly burnt what articles of that manufacture they already possessed.

From statistics just to hand it appears that in 1912—a particularly unsettled year—leather valued at about one million sterling was imported from China, so that apart from competition with the local manufacture, there is obviously an opening for the enterprise of the leather trade.

THE RUSSIAN LEATHER INDUSTRY.*

The past year 1913 has not been an unfavorable one for the leather trade in Russia. At its commencement all manufacturers were suffering more or less severely from the effects of the financial crisis of the years 1911 and 1912; especially 1912, when the number of failures in the leather trade was nearly unprecedented. In February, prices of hides and skins began to advance, and continued to do so until during August, September and October, tanners were then paying prices which have never before been reached in Russia. Fortunately, however, the demand for the manufactured product, particularly sole leather, was very great, and proportionately increased prices were obtained without very much difficulty, as tanners were mostly quite without any stock. Towards the end of the year this demand fell off, and the prices of hides were also slightly easier, although it is practically certain that the low prices of former years, both in hides and leather will never again prevail in Russia. The reason for this is that the increase of domestic animals has not kept pace with the increase of the population, land is getting dearer, and is increasingly cultivated, and the export of cattle continually increases. Whereas formerly, cattle were shipped

* Anonymous in *Leather Trades' Year Book*, pp. 139-47.

Digitized by Google

solely to Constantinople, there is now a large demand in Berlin, resulting since the meat famine in Germany, when Russian cattle were first exported to that country.

In the year 1910 the number of animals was about as follows:

	Millions
Oxen and cows	51
Sheep	80.5
Horses	35
Goats	5

This was followed by the disastrous year 1911, with a famine in certain parts of Siberia, when thousands of cattle were slaughtered and sold for less than the mere value of the hides, or starved to death; 1912 was much more favorable, owing to there being better pasturage, and in many instances the losses were to some extent recouped; 1913 has, although no statistics are yet available, doubtless been still more favorable, but with a population of 167 millions it will be recognized that Russia cannot long continue to export hides and to supply her own wants.

The imports of sole leather into Russia have long since practically ceased, the high duty making foreign competition impossible. The great bulk of vegetable-tanned upper leather for peasants' sapoguies or top-boots is also made in the country, but an enormous quantity of chrome-tanned leather, box-calf, glace kid and sheep, still comes from abroad, principally from Germany (which has the bulk of the trade), France and the United States. The tariff rates on this article are unfavorable to the home manufacturers, for whilst the duty on the chemical materials used, ranges from 45 per cent. to 100 per cent. ad valorem, that on the finished product, which is still assessed by weight, amounts to only some 6 kopecks (3 cents) per foot. This will doubtless be changed in 1917 when present convention-tariff expires.

The use of extracts, particularly quebracho is increasing enormously, as most of the larger tanners now tan either entirely or partially by the aid of drums. It is no surprise, that with the high duty of 75 kopecks per pood (1 cent per pound) on tanning extract, that the number of extract factories is being continually added to, although chiefly foreign capital is employed. The home-made article is, I think, equal in most cases

Digitized by Google

to that from abroad, of which latter Germany supplies the greatest quantity. As the price of the home product is in no instance lower than the foreign article, and there is no duty on imported wood, a pretty good return on the money invested should be obtained by the local manufacturers. With the gradual extinction of small tanneries, more especially the makers of leather in villages, and the concentration of the industry in large yards, tanning from 1,000 to 4,000—5,000 hides weekly, the use of machinery is enormously increasing, the whole of which, with the exception of tanning drums comes from Germany or America.

In the matter of labor saving devices Russian tanneries are, I think, well in the forefront. This may be perhaps owing to some extent to the fact that the technical directors of a large proportion of the leather factories, as well as of other manufacturing industries, are foreigners. The Russian does not take readily to the drudgery of an industrial training. Every parent, not only of the wealthier, but of the middle and frequently of the working classes strives to give his son a university education. The greater proportion of these young men adopt a professional career, or accept military or other government appointments which are probably the worst paid in the country, even taking the special emoluments into consideration. Exceptions are those cases, where their fathers are proprietors. But even in these cases the technical management is more frequently left in the hands of foreigners. It may be said, that Russia offers many attractions to the foreign technical man; salaries are generally good, life and work are easier, and if the purse is fairly ample, there is less restriction on the liberty of the subject than in other European countries. The sole drawback is the irritating formalism of the army of "Tshinovniks" (officials), always seeking whom they may devour, and whom not to propitiate would spell disaster. Very rarely will it be found, that a foreigner once settled for two or three years in the country is ready or anxious to leave.

With regard to the working man:—In spite of all that is written I do not honestly think that his lot in the large towns is, on the whole, worse than that of the workers in other Euro-

Digitized by Google

pean countries, with possibly the exception of housing accommodation. Hours are to-day much shorter than formerly, food is cheaper than in England (vodka, unfortunately, also). Provision is made for compensation in case of accidents; medical attendance and medicines are provided by the employer; and last year the new Insurance against Sickness Act came into force.

The principle of the Workmen's Compensation Act is much the same as everywhere else, with perhaps the exception that the litigation of which Judge Parry speaks in his: "What the Judge saw" is almost entirely avoided, owing to the great power, which lies in the hands of the factory inspectors, whose influence is on the weaker side, and whose will generally prevails with both insurance company and employer.

Within the next few weeks a new system of government-controlled insurance companies comes into force. Up to the present they have more often been capitalized by the employers under a mutual system, and premiums have varied with the expenditure. It is difficult to foresee just how the new scheme will work, as the tariff does not become fixed until after some months' working; employments will be grouped according to their relative risks, and a much stricter system of supervision will prevail, in order to ensure that all machinery be properly guarded, and so on. A very interesting feature, one which clearly shows the minds of the party at present in power at St. Petersburg is, that only Russian subjects will be insured in these government controlled offices, and although employers will be compelled to make the same provision for foreign subjects employed by them, they must either effect insurance with private companies at presumably higher rates or take risks themselves. This seems to me a very unpleasant feature which I am sure cannot long remain, for the vast army of German workers and employers are prefectly certain to get prompt representation made in proper quarters that such distinction is decidedly unfair and distasteful.

For many years now workers in Russian factories have been entitled to medical attendance and medicines at the expense of the employers; and usually each factory has engaged its own

Digitized by Google

special doctor. In August, 1913, however, the new insurance against sickness and accidents came into effect without any of the political recriminations and excitement which marked the coming into force of the famous act in England; political meetings being absolutely forbidden. The principles of the act, so far as I know, are quite novel. In the first place no government grants are allowed, and in the second place, within wide limits the entire control is in the hands of the workers themselves.

The above sum includes medical attendance to families of receive compensation to the extent of no less than half his regular wages in case of sickness.

Any factory employing not less than 200 men can have and control its own organization; factories having less than that number must form groups. A general meeting of the men is held, deputies are chosen from the workmen, and a staff to arrange the rate of the contribution, remuneration of secretary, committee, and the amount of compensation, and it is decided whether the wives and families of the men shall be included in benefits or not, etc., etc. To every 1 per cent. contributed by the men, the employers must add ⅔ per cent. Printed cards are supplied to the employers, who must fill in the date and duration of illness, upon which the factory doctor must add the special medical details. The working of the act has been of too short duration yet to give any definite statistics, but the following balance sheet showing details of its working in one large leather works in which it was decided to render medical and other aid to families of the employed, will be perhaps interesting.

INSURANCE AGAINST SICKNESS ACT.

Factory Balance Sheet, 17th of August to 31st of December, 1913.

Credit—	Roubles	*Debit*—	Roubles
Received 1 per cent. of wages from staff	130.63	Placed to reserve	68.22
From workmen	663.37	⅔ of wages paid to employees during sickness	875.71
From employer, ⅔ per cent	537.41	Doctor's fees and medicines	271.22
Fines	1.73	Expenses, fees, etc	113.46
	1,333.14	Funeral expenses	87.00
Presented by employer as nucleus to the fund	424.00	Balance on hand	341.53
	1,757.14		1,757.14

Digitized by Google

The above sum includes medical attendance to families of workmen, but, as will be seen, the expenses amounted to more than the income, and at a general meeting of workmen it was decided to increase the contribution to 1½ per cent. of wages, which would mean by law, a corresponding increase on part of employer. This will, it is believed, allow of a slight increase of the benefits including monetary aid in cases of the confinement of contributors' wives, also funerals, etc. In the case of employees receiving more than 125 roubles a month, contributions can only be levied and benefits paid upon said sum, no matter what may be the actual amount of salary.

It will be seen that the amount levied, *viz.*: I per cent. on wages of workmen with payment of two-thirds of wages in case of sickness was insufficient and a levy of 1½ per cent. is now made, with, of course a proportionate increase of levy on employer. In this instance there are no administration expenses whatever, the firm providing committee-room, etc., and the clerical work is undertaken without payment. This is not always the case, but in no case are the costs of administration more than nominal, and simply include the payment for a committee-room, secretary's salary, and small sum to the working and control-committee, at the most.

On the whole it must be said that, at present at least, trade, and the leather trade especially, in Russia is in quite a healthy condition. The workers are better paid than formerly, although this is like elsewhere, depreciated by increased cost of living. The epidemic of strikes seems for a time at least to have stopped. The government, to judge from circulars being issued, are seeking information and suggestions for the improvement of the industrial position, and seems much more alive than formerly to the importance of fostering Russian industries.

The greatest want now for the working classes is some sort of insurance against unemployment. At the present time it may be said, the position of the man or woman unable to find work is deplorable. He has absolutely nowhere to go or nothing to depend upon, and often literally starves with his children. Organized philanthropy, as understood in England, is practically

Digitized by Google

unknown, and no serious attempt has yet been made, either by the government or the municipality to cope with the question.

There are no workhouses, few or no trade unions, and labor itself is quite unorganized. The Russian, if properly paid, properly trained and properly treated, is an excellent craftsman and in nowise inferior to workmen of other countries, and with the slow but sure growth of education and prohibition of the Vodka trade, will have to be reckoned with in the world's markets as, I think, statistics lately published in Mr. Whelpton's World-papers, sufficiently show.

THE DANISH LEATHER INDUSTRY.*

By Max Ballin (Copenhagen.)

During the last 20-30 years the leather-manufacturing industry has undergone considerable change in Denmark. The industrial development of this old-fashioned trade, combined with the technical revolution in the art of leather-manufacturing, have made it almost impossible for the small tanyard to exist. The astonishing fluctuations in the prices of raw-hides have also assisted towards the concentration of the trade, as it was quite impossible for the small tanner to stand the risk of loss, due to the constant rising and falling of the price curves.

In 1894 Danish cow-hides had a value of 2½d. per lb.; their present value is about 6½d.! The price of leather has risen in this country, as in others, but it is now quite a necessity to take full advantage of all technical and chemical knowledge available, in order to make it possible to carry on this business; and it is only a small number of tanners who can afford to do this. From 1900 to 1907 about 40 small country-yards were closed, and since 1907 another 10 tanyards have stopped working.

The modern method of selling all native hides by public sale, has also altered the situation enormously in disfavor of the small tanner, who formerly bought his hides directly from the butcher or the farmer, at a proportional low price, turned it into leather in his pits in the old-fashioned way, and sold it again at

* *Leather Trades' Year Book*, pp. 175-7.

Digitized by Google

his door. Nowadays we find only a few tanneries in Denmark, but though the country only has half as many inhabitants as London, there are some rather important factories working under perfectly modern methods, using extracts, and also tanning a quite important quantity of leather by the modern chrome process. The product is good and, especially the sole-leather, very suitable for the shoe manufactories which are highly developed in this country, producing about £700,000 value, and employing about 2,500 hands.

Most of the sole-leather is purely drum-tanned and consequently produced in a very short time. It is difficult for the Danish leather-manufacturer to use Danish hides for sole-leather as these are too light, and can only be tanned to advantage for harness-leather, box-sides, etc. In consequence large quantities of La Plata and Australian hides are imported for the production of sole-leather. The greatest portion of the Danish calfskins are exported, chiefly to United States. One large Danish firm of tanners has started yards in Germany and Sweden; these are worked on the same modern principles and successfully compete with the other manufactories in those countries, which is a proof of the good quality of the products and the rational methods of work.

The Danish import duty for sole-leather is about 10 per cent. of the value, and importation on this account is nearly prohibitive. On upper-leather the duty is very low, and in consequence a good deal of continental chrome-tanned leather is imported; also the United States do good business in glacé-kids, which are not manufactured in Scandinavia. A quantity of the American importation is re-exported to Sweden, Norway, and Russia; and on the whole, Copenhagen with its free port is an important center for the leather trade in the adjoining countries.

Dealing with the question of labor, and the agreements between workmen and employers, Denmark is on a very high level. The leather trade has contracts running, usually in periods of 5 years, thereby practically securing an immunity from strikes or lock-outs during the tariff period. The daily working time is 9½ hours, and the wages for a tanner about 6 or 7 shillings a day, and about 6d. per hour for laborers.

Digitized by Google

In accordance with the system of collective agreements between the organizations, the manufacturers and their customers have also different unions, who deal with any important commercial questions, which are settled to their mutual interest; and a permanent committee is formed who deal with bankruptcies, etc. On questions of duty and taxes the whole trade is represented by an executive committee, so that it is possible to put forward representations to the government with a much greater weight than would be possible by single representation.

Danish tanners were quick to realize the importance of scientific knowledge for the trade, and founded and supported a "Research station" for the purpose of furthering the scientific study of the industry. The first head of this Institute was the well-known leather trade chemist, Mr. V. Boegh, who, when he died in 1910, left behind him 20 years record of scientific work on the problems of leather manufacturing. His name was also known in England and on the continent; an honest, modest, and clever chemist, who was in constant communication and collaboration with English and German men of science who specialized in leather trade chemistry.

Generally speaking the year 1913 has not been a very prosperous one for the Danish leather trade as it has not been found possible to raise the price of finished leather to a figure corresponding to the rise in rawhide prices.

THE HEAVY LEATHER INDUSTRY OF HOLLAND.*

By J. L. Van Gijn.

In an article in the Year Book in 1908, I dealt with the leather trade of Holland; six years have elapsed since then, and in these progressive times this means a considerable change in such an industry. The old-fashioned bark-tanner, even if he employs materials such as mimosa-bark, myrobalans and valonia, is having a very hard time in Holland. Hides have gone up in price all the world over, but leather has not followed in the same proportion. Using weak liquors and bark, it is not possible to

* *Leather Trades' Year Book*, pp. 178-80.

Digitized by Google

get a high yield in the weight of leather, and although the old fashioned pit—and bark-tanned leather—possesses decided advantages as regard light weight and strong wearing properties for the boot-manufacturer, the price the latter will and can offer, is too low to leave a decent margin for the tanner. Extracts are being employed more and more with the effect of reducing the time of tanning in the pits and also resulting in increasing the weight of finished leather.

Strange ideas as regards the methods and the propriety of using extracts still exist among the country tanners. Although the leaching of barks and the using of the liquors so obtained is identical with making up the strength of the liquors by dissolving ready made extract, some tanners look still upon extracts as a form of weighting the leather. Some time ago a tanner told the writer that a certain well-known brand of solid valonia-extract was offered to him as a secret material for getting weight, and as this has also happened to other tanners it is easy to understand that this material is now looked upon by many tanners in this country as an adulteration.

Thanks to the spirit of co-operation which exists among the brotherhood of tanners in different centers, tanning materials are nowadays bought by tender, thus enabling the tanner to get fair market-values, which would not be possible if each small tanner bought for himself.

The older fashioned sole leather obtained from prime salted B. A. hides and laying away in pits for at least twelve months is going out of favor because of the comparative low price obtained for the finished leather, leaving little profit for the tanner.

Many tanners have adopted more modern methods for the manufacture of sole leather, and, strange to say drum-tanning is being taken up by the majority of them. The drum-tanning process has of course great advantages compared with the older systems, as it enables one to turn out sole-leather (called always "vache-leather") in a much shorter time; about 1 to 2 months from the raw hide to the finished leather. By using strong extract liquors in the drum a high yield in leather is obtained. The turnover is thereby considerably increased. The majority of tanners in this country who have adopted drum-tanning have

Digitized by Google

been successful. Owing to the introduction of light colored extracts and the application of water-soluble oils no bleaching is necessary so that the leather does not suffer in quality on this account.

Sulphite-cellulose extracts are used fairly frequently nowadays. Although the actual tanning value of these wood extracts is small compared with the high density of the extracts, they are employed as filling agents. The question as to whether a leather containing sulphite-cellulose extract may be regarded as adulterated remains still open, and the writer hopes that the next conference of the I. A. L. T. C. in Vienna will settle this question.

Two kinds of sole-leather which are taken up so largely by the English leather manufacturers, *e. g.*, the so-called red "Hemlock" leather, and chrome sole-leather, are not manufactured as yet in Holland. Comparatively speaking little hemlock leather is imported, so the want of red leather is not felt in the same way as in England. On the other hand it may be said that, as there are no duties on leather, a considerable quantity of cheap foreign sole leather is dumped on the Dutch markets, so there is no reason why a leather should not be made which is cheap enough to compete against the imported leather.

As regards the manufacture of chrome sole leather, the failure of a Dutch firm who started some years ago manufacturing this leather, has discouraged the manufacture of this new product, but sooner or later chrome sole-leather will be tried, especially as chrome tanning of upper—and other leathers—is making rapid strides in this country.

PURE SALT AND ITS VALUE TO THE LEATHER INDUSTRY.*

By Andrew Turnbull, Ph.D.

Salt is undoubtedly the most suitable material, easily procurable in sufficient quantity for the curing of hides and skins, to preserve them in a fit condition for tanners' purposes. It is very widely distributed throughout the world as the principal

* *Leather Trades' Year Book*, pp. 181-4.

Digitized by Google

solid constituent of sea water, and in immense deposits as rock salt formed by the evaporation of sea water cut off from the ocean by volcanic upheaval. As sea water contains other salts in solution besides sodium chloride, and rivers keep bringing in fresh impurities, the deposited salt is never quite pure, although the tendency is for the least soluble salts, such as gypsum and chalk to separate first, then the common salt, and on the top of this the more soluble salts of potassium and magnesium.

Rock salt as it is mined may be nearly colorless, light yellow or dark brown according to the nature of the impurities. Commonly it contains about 98 per cent. sodium chloride, the remaining 2 per cent. being chiefly calcium sulphate, sodium sulphate, magnesium chloride, and some oxide of iron. Portugal and countries on the shores of the Mediterranean obtain salt by evaporating sea water in large pans exposed to the heat of the sun, whilst in cold countries like Russia and Sweden the bulk of the water is removed by freezing and the resultant mother liquor is boiled down to yield a very impure salt containing no more than 80 per cent. sodium chloride. In this country the chief source of supply is in the form of a nearly saturated solution of brine which is pumped to the surface and evaporated to obtain crystals of salt containing about 97 per cent. sodium chloride, the rest being chiefly calcium sulphate, sodium sulphate and magnesium carbonate. Traces of ferrous carbonate are eliminated by exposing the brine to the air before evaporation.

The fine grained salt obtained from brine by rapid boiling is probably the most suitable common salt which has been used for the curing of hides and skins. Some time ago I had the privilege of viewing a works near Lymm, Cheshire, where brine is chemically treated before evaporation and a very fine grained salt is obtained which analyzed as follows:

Magnesium sulphate	.0049
Magnesium carbonate	.0144
Insoluble matters	nil
Sodium chloride	99.9807
	100.0000

This is really pure sodium chloride, and it would be difficult to find any other article of commerce of such remarkable purity.

Digitized by Google

In many countries, for purposes of taxation, the salt used in manufacturing processes has to be denaturized to render it unfit for human consumption. Materials have been used for this purpose which possess objectionable characteristics when the salt is used for curing skins. Those containing iron or alum in appreciable quantities are most objectionable, and it has also been shown that the blue oil obtained as a residue from petroleum frequently causes stains on skins. Apparently 4 per cent. on the weight of the salt of dry soda ash is the most suitable denaturizing agent for salt that is to be used in curing hides and skins.

Stains on salted skins have usually been attributed to impurities in the salt used, and it is only lately that attention has been drawn to other influences. Dr. H. Becker[1] has described stains that were due to chromogenic micro-organisms, the growth of which is encouraged by the filthy conditions common before and after curing, the sparing of salt so that the thicker places are not sufficiently cured and are liable to putrefy; and the storing of the skins in a damp warm atmosphere. He strongly recommends that only clean finely powdered salt should be used, and its antiseptic properties assisted by previously dipping the skins in a ¼ per cent. solution of mustard oil.

Dr. Pæssler[2] has shown that the addition of 4 per cent. dry soda ash to the salt used in curing calf-skins makes the formation of salt stains very unlikely.

Dr. Baldracco[3] has added 5 per cent. borax to the salt used and now recommends 1 per cent. sodium fluoride instead for the same purpose.

W. Eitner refers to stains caused by unsuitable denaturizing materials such as alum and petroleum, and he strongly condemns too late salting, sparing salt, and bundling hides immediately after salting and before the brine has run away. The salt acts as a dehydrating agent and the brine carries away lymph liquid which very readily putrefies. The salt which remains in the fibers acts as a mild preservative.

[1] *Collegium*, 1912, p. 408.
[2] *Collegium*, 1912, p. 397.
[3] *Der Gerber*, Jan. 2, 1911, p. 874.

Digitized by Google

J. H. Yocum[4] remarks that salt stains are caused by the action of salt on the blood left on the skins and possibly too high a temperature during curing which would assist both chemical and bacterial action.

Dr. Georges Abt[5] has attributed certain stains to small quantities of calcium and magnesium sulphates, always present in ordinary salt, reacting chemically with phosphoric acid, naturally present in combination in hides, to form phosphates which produce discoloration with the acid of iron from the salt or blood on the skins. He also states[6] that bacteria act on the iron in blood to cause stains, and describes a chromogenic organism capable of staining.

L. L. Lloyd[7] states, that bacterial stains are more readily formed when the salt used contains the usual small quantities of calcium and magnesium sulphates than when pure salt is used. He believes that hide-substance reacts with neutral salt to form hide-acid substance and hide-alkali substance, and that sodium sulphate acts more powerfully than sodium chloride. He also holds that bacteria develop more readily in ordinary salt containing the usual traces of sulphates than in pure salt. Hide-alkali substance is more soluble in water than hide-acid substance and this solubility is greatly increased if any putrefaction has taken place.

The writer has been supplied with figures which support the contention that the use of pure finely powdered sodium chloride under proper conditions not only avoids the formation of stains but also greatly reduces the solution of hide-substance during storing and subsequent soaking. The figures require further confirmation, and it would be advantageous if tanners could make comparative trials with packs of goods, curing some with ordinary salt and others with pure salt, and carefully noting the resulting pelt and leather weights.

[4] *Journal American Leather Chemists' Association*, Vol. 8, p. 22.
[5] *Collegium*, 1912, p. 388.
[6] *Collegium*, 1913, p. 439.
[7] *Collegium*, 1913, p. 188.

Digitized by Google

ABSTRACTS.

Second Report of the International Commission for the Preservation, Cure and Disinfection of Hides and Skins. *Collegium*, 1914, 267-79. A long list of articles on the subject, published since the first report in 1912, opens the present report. Improved methods of destroying the warble fly include injecting one drop of iodine solution into the tumor, or a like quantity of formalin. A heated lancet or needle may be used to pierce the larvae. The commission recommend, that the fell-mongers' collecting limes be abandoned, and that the skins be put instead into water containing beta-lysol or other suitable antiseptic. On the subject of salt-stains, reports by Becker and Abt are given, and a note on the value of pure salt. These have all appeared in abstracts in the JOURNAL. On the subject of disinfection, quotations are given from Abt's report, a long abstract of which appeared in the June, (1914) JOURNAL.

Surface Combustion. WILLIAM A. BONE. *Journal of the Royal Society of Arts*, July 31, Aug. 7, Aug. 14, 1914. These lectures describe a new sort of gas burner which is destined to be of great use in many lines, and is of special interest to chemists. In one typical form the gas, mixed with air in the right proportions for complete combustion, is led into a chamber, one face of which is of porous refractory material. The mixture issuing from this porous diaphragm is lighted, and as the diaphragm becomes hotter the flame diminishes in size. When the refractory diaphragm is incandescent on the surface, the flame disappears entirely, combustion being complete by the time the gas reaches the surface. Such a diaphragm may be placed at any angle, and is a very convenient and efficient source of radiant heat. Thick liquids may be evaporated without sputtering by placing such a disk, hot face down, over a vessel containing the liquid. Other modifications are adapted for heating muffle furnaces and for many other uses.

Some Practical Observations on the Preparation of Lime—Arsenic Paints. R. FARADAY INNES. *J. S. C. I.*, vol. 33, pp. 578-9. Text books of tanning recommend that the lime—arsenic paste used for unhairing be made by first sprinkling red arsenic over the lime, adding water and stirring the mixture. The author finds that this method does not give a uniform product, nor the best results. He recommends that the lime be slaked first, using water enough to permit the mass to boil without violence, so that there shall be no local overheating, and the arsenic added as soon as the slaking is complete, the whole being then very thoroughly stirred.

Definition of Adulterated Leather, Union of South Africa. *Board of Trade Journal*, July 2, 1914. The limit of mineral ash is set at 3 per cent. for vegetable-tanned leathers and for glucose, etc., at 2 per cent. Chrome and combination leathers must not contain barium, epsom salts, lead or tin compounds nor sodium sulphate.

Digitized by Google

Preparation of a Fat Liquor. ANON. *Conceria*, 22, 11. In this method an emulsion of oil is used, the advantage being that the oil is completely absorbed in its natural condition (without the necessity for saponification). An amount of fat liquor equal to 4-5 per cent. of the weight of the hides is used; this amount corresponds to 2-2.5 per cent. oil. The fat liquor is prepared by dissolving 100-150 grams of soda crystals in .5 liters of soft water (condensation water) at 70° and mixing well with 150-200 grams of potato paste which has been well kneaded with warm water; one liter of castor oil (previously heated) is then added with constant stirring. The other oils and fats (first rendered fluid by heating) are then added with slow stirring; for a leather well loaded, of good texture and softness, and of moderate brightness it would be advantageous to use 2 kilos of fish oil or *dègras* (or a mixture of both) and 1-2 kilos of neats-foot and paraffin oil. Fish oil and *dègras* produce softness, while neats-foot and paraffin oil produce clearness and brightness, so that the relative proportions of the oils should be governed by the qualities desired. In order to produce an odor similar to that of Russia leather, 100-200 grams of birch oil may finally be added to the emulsion. After being well shaken for several minutes, the mixture should not, if properly prepared, float on milk and should not deposit oil or fat; a perfectly homogeneous mixture should be formed when a tumbler of the emulsion is poured into a pail of warm water. If this is not the case, this condition may be corrected by adding a little tannin and finally some soda; the latter may be increased as needed, but should not exceed 200 grams. For preparing a large amount of fat liquor an agitator may be advantageously employed. The fat liquor should not be heated to boiling and should also be protected from cold (in order to prevent the separation of oil); it should be kept in a moderately warm location. The fat liquor should be mixed only with warm (not boiling) water and should be applied only to "warmed" hides. H. S. PAINE.

Method of Brightening Hides with Latic Acid. *Conceria*, 21, 507. Lactic acid is being used to a great extent to replace sulfuric acid in the brightening of hides preparatory to dyeing because of the corrosive action of the latter acid. The general procedure consists in preparing a bath of 2 per cent. lactic acid in warm water and immersing the hides or applying the diluted acid with a brush. The action of the lactic acid is more uniform if the hides are first moistened. If acid dyes are used, the leather may be dyed directly after the application of lactic acid. For basic dyes it is usually desirable to wash out the acid in clear water; this is not necessary in all cases, however, since some basic dyes give better gradations of color on an acid surface.

This question should be determined in each case by preliminary experiments on a small scale. For ram skins it is desirable to add a little alum to the lactic acid solution and, if the skins are very greasy, they should first be immersed in clear water, then in a dilute solution of soda crystals, and finally rinsed with water before treating with lactic acid.

Digitized by Google

In addition to its use preparatory to dyeing to obtain gradations of color, brightening of skins with lactic acid is of value for many other purposes; *e. g.*, the black color of glove leather is more uniform if the skins are first brightened with acid. All the preparations for this purpose which are on the market owe their efficacy to sulfuric or lactic acid and are, furthermore, more expensive than the latter. H. S. PAINE.

Decolorization of Oils and Fats. ANON. *Conceria*, **22**, 55. A patent obtained by A. Metz and P. L. Clarkson provides for the decolorization of all oils and fats (both drying and non-drying) by means of hydrosulfites, the latter including the sodium and zinc salts as well as combinations of the hydrosulfites with formaldehyde, etc. The color of the non-drying oils is destroyed and cannot be restored. The procedure is illustrated by the following examples. (1) Two hundred parts of corn oil are mixed with 500 parts cold water containing 15 parts of sodium hydrosulfite. The mixture is kept agitated in a closed container for 10 hours and then allowed to settle. The yellow color gradually becomes less pronounced and completely disappears in 32 hours. (2) Two hundred parts of corn oil are mixed with 600 parts of cold water containing 10 parts of sodium hydrosulfite; the mixture is well agitated and then heated to 70° C. After cooling the mixture is allowed to settle and the same change in color is observed as in the 1st example. (3) Two hundred parts of linseed oil are mixed with 600 parts of cold water containing 20 parts of sodium hydrosulfite. After mixing well and allowing to settle for 32 hours, the color is discharged without any change in the oil being observed. After decolorization the oil may be removed by decantation; any residual oil may be recovered by means of a suitable solvent, *e. g.*, petroleum ether. H. S. PAINE.

Softening of Dried Hides. ANON. *Conceria*, **21**, 507. Pure, fresh water should be used for each lot of hides and the containers should be kept scoured and free from filth. For softening 500 hides of medium size 1-2 kilos of sodium monosulphide should be dissolved in boiling water and added to the water used for moistening. After the hides have become thoroughly softened, they should be rinsed with pure water before liming. Sodium monosulphide improves the quality of the hides, making them firmer and more flexible and imparting a finer grain. It is advantageous to change the water several times during the process of softening. H. S. PAINE.

Rapid Tanning Process. ANON. *Conceria*, **22**, 124 In this rapid tanning process baths are prepared, viz.: in bath 1, tanning extract is dissolved in water until the density is 1° Bé and $BaCl_2$ is then added until the density reaches 5° Bé; baths 2, 3 and 4 are prepared by dissolving tanning extract until the densities are 2°, 3° and 4° respectively and then adding the same absolute amount of $BaCl_2$ as above. The dehaired and cleaned hides are suspended for several days in bath 1 and are then placed successively in baths 2, 3 and 4. H. S. PAINE.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. IX OCTOBER, 1914 No. 10

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1914, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VEITCH, } . . . Past Presidents

OFFICERS, 1913-'14

PRESIDENT—W. K. ALSOP, Ridgway, Pa.
VICE-PRESIDENT—C. W. NORRIS, 80 South Street, New York, N. Y.
SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y
LLOYD BALDERSTON, Ridgway, Pa.
C. R. OBERFELL, Harrisonburg, Va.
T. A. FAUST, 323 Academy Street, Newark, N. J.

ELECTIONS.

ACTIVE

Frank H. Yocum, 168 Mill St., London, Ontario, Canada.

ASSOCIATE.

Sanya Miyoshi, 1162 Senjunakagusni, Tokyo, Japan.

CHANGES OF ADDRESS.

R. W. Griffith, to 510 Paul Jones Bldg., Louisville, Ky.
R. H. W. Lord, to Gorham, Me.
George F. Rumpf, to 4225 N. Ninth St., Philadelphia, Pa.
V. Y. Shewade, to 689, Sadashio Peth, Poona City, India.

Digitized by Google

ELEVENTH ANNUAL MEETING.

The Eleventh Annual Meeting of the American Leather Chemists Association, in conjunction with the Annual Meeting of the National Association of Tanners, will be held at the Hotel Sherman, Chicago, Ill., on Wednesday, Thursday, Friday and Saturday, October 28th, 29th, 30th, and 31st, 1914.

Rates at the Hotel Sherman are as follows:

Room with bath—$2.00, $2.50, $3.00, $3.50, $4.00 and $5.00.
Room with bath for two—$3.00, $3.50, $4.00, $4.50, $5.00 and $6.00.
Suites of two rooms, 2 persons—$5.00, $7.00, $8.00 and $10.00.
Suites of two rooms, 4 persons—$7.00, $9.00, $10.00 and $12.00.

The program as arranged to date is as follows:

Wednesday Morning (in Grey Room).
A. L. C. A. 9.00.
President's Address.
Secretary-Treasurer's Report.
Committee Reports.

Wednesday Afternoon (in Grey Room).
A. L. C. A.
"Tannery Sewage," A. Roth.
"Color Valuation of Tanning Materials," George A. Kerr.
Discussion.

Thursday Morning (in Grey Room).
A. L. C. A.
Committee Reports.
Discussion.

Thursday Noon.
Luncheon.
Round Table Discussions.

Thursday Afternoon (in Grey Room).
A. L. C. A.
"The Bating of Hides and Skins," Dr. Allen Rogers.
"Available Tannin in Liquors of Various Strengths," Thomas A. Faust.
Discussion.

Thursday, 6.30 P. M.
Executive Committee T. N. A. T.
(Group meetings also to be scheduled.)

Digitized by Google

Friday Morning (in Grey Room).
A. L. C. A.
"Spruce Extract," Sigmund Saxe.
"The Clarification of Leather Extracts for the Determination of Reducing Sugars," F. P. Veitch.
Discussion.
Friday Morning (in Louis XVI Room).
T. N. A. T.
General Meeting.
Friday Noon (in Crystal Room).
Lunch Allied Trades.
Friday Afternoon (in Louis XVI Room).
Joint Meeting A. L. C. A. and T. N. A. T.
Discussion Tanning School, etc.
Friday, 6.30 P. M.
Complimentary to A. L. C. A. and Theatre.
Saturday Morning (in Grey Room).
A. L. C. A. Executive Session.
Election of Officers.

H. C. REED,
Secretary.

CLARIFICATION OF LEATHER EXTRACTS FOR THE DETERMINATION OF REDUCING SUGARS.

Further Experiments with Special Reference to the Comparative Merits of Normal and Basic Lead Acetate.

By F. P. Veitch[1] and J. S. Rogers.[2]

It has been the general experience of analysts who have worked on the problem, that the method of clarifying leather extracts[3] for the determination of reducing sugars, suggested by this Bureau, and adopted by the American Leather Chemists Association,[4] has given entirely satisfactory results, while the Von Schroeder method has seldom given accurate results; the results in practically all cases being decidedly low.[5] But one exception

[1] Chemist in Charge, Leather and Paper Laboratory, Bureau of Chemistry.
[2] Assistant Chemist, Leather and Paper Laboratory, Bureau of Chemistry.
[3] *J. A. L. C. A.*, Vol. 4, p. 272, 1909.
[4] Made official January, 1914, *J. A. L. C. A.*, Vol. 9, p. 2, 1914.
[5] The cause for these inaccurate results will be brought out further on in the paper.

Digitized by Google

to this general experience has come to notice in the last four or five years, and this exception is the experience of Paessler[6] who co-operated in the work of the Leather Analysis Committee of the American Leather Chemists Association in 1912. Paessler found that the results by the American Leather Chemists Association method were high, while the results by the Von Schroeder as he used it were satisfactory.

The essential difference between these two methods is that in the Von Schroeder procedure basic lead acetate is used as the clarifying agent, while in the American Leather Chemists Association method normal lead acetate is used.

The comparative merits of these two reagents as clarifiers of sugar solutions has been the subject of numerous investigations, and further work on the subject would perhaps have been unnecessary, had there been more data available as to their use in the clarification of leather and tanning material extracts, and it therefore seemed worth while to work especially on these materials.

The objects of this paper are therefore: (1) to explain the differences in the results obtained in the co-operative work on leather analysis in 1912 by Paessler and other members of the committee, (2) to determine whether the joint use of basic lead acetate as clarifier, with potassium oxalate as precipitant, is the cause as suggested by Paessler, of the low results obtained, and if this is not the case (3) to determine the cause of the low results when basic lead acetate is used as clarifier for leather extracts; and also to study and test out comparatively the Von Schroeder and the American Leather Chemists Association methods for clarification of leather extracts for the determination of dextrose.

Explanation of Differences in Results.—The results[7] of the determination of sugars in leather extracts obtained by Paessler, co-operating with the committee on leather analysis for the American Leather Chemists Association in 1912, were not in agreement

[6] *J. A. L. C. A.*, Vol. 8, p. 136, 1913.

[7] Received too late to be published in the committee report, but appears in *J. A. L. C. A.*, Vol. 8, p. 136, 1913.

Digitized by Google

with those obtained by the committee,[8] This difference although small was quite uniform for all results. A careful examination of the results led us to believe that Paessler had used the "Allihn" table instead of the "Munson-Walker" table for his calculations. It was learned after communication with Paessler that he had used the "Allihn" table for the calculation of his results. After calculating Paessler's results as received back to Cu_2O using the "Allihn" table and then calculating to dextrose using the Munson-Walker" table it was found that they agreed well with those obtained by the A. L. C. A. committee. The results as received from Paessler and as they appear after recalculation, together with the maximum and minimum results obtained by the A. L. C. A. Committee, are given in Table I.

Does the joint use of basic lead acetate as clarifier and potassium oxalate as precipitant cause low results for dextrose?—Since it has been suggested[9] that the joint use of basic lead acetate as clarifier with potassium oxalate as precipitant is the cause of the low results which have been obtained in many cases where basic lead acetate is used, we have studied this question with the results shown in Table II. The leather extract was prepared by extracting the hemlock leather (15 g. per liter) used for the A. L. C. A. Committee work for 1912. Reducing sugars were determined on the original extract and on the extract after the addition of 8 per cent. of dextrose on the basis of the leather. Magnesium sulphate was added to the extract in a few cases to learn what effect the presence of this salt would have upon the amount of sugar found. In some of the experiments basic lead acetate prepared according to Von Schroeder was used, and in other cases a saturated solution of Horn's basic lead acetate. Sodium sulphate was employed to remove the excess of lead in all cases except in experiments Nos. 7 and 8 in which potassium oxalate was used. Since the A. L. C. A. Committee report showed low results in all cases where clarification has been made by addition of 25 cc. of basic lead acetate to 200 cc. of leather extract (15 g. per liter) and where the excess of lead was removed by means of

[8] *J. A. L. C. A.*, Vol. 7, p. 645, 1912. This report also gives references to many important articles on clarification of sugar solutions for the determination of reducing sugars.

[9] *J. A. L. C. A.*, Vol. 8, p. 136, 1913.

Digitized by Google

TABLE I.—PAESSLER'S[1] RESULTS CALCULATED BY "ALLIHN" AND BY "MUNSON-WALKER" TABLES.

Method of clearing	Original results as reported by Paessler			Results as recalculated from Munson-Walker table			Maximum and minimum results as obtained by A. L. C. A. committee		
	25 cc. Normal lead acetate per cent.	25 cc. Basic lead acetate per cent.	25 cc. Normal lead acetate plus zinc oxide per cent.	25 cc. Normal lead acetate per cent.	25 cc. Basic lead acetate per cent.	25 cc. Normal lead acetate plus zinc oxide per cent.	25 cc. Normal lead acetate per cent. Max.-Min.	25 cc. Basic lead acetate per cent. Max.-Min.	25 cc. Normal lead acetate plus zinc oxide per cent. Max.-Min.
Oak leather extract plus 8 per cent dextrose ..	8.42	6.65	8.65	8.04	6.29	8.25	8.25-7.82[2]	7.13-5.91	8.15-7.64
	8.32	6.50	8.30	7.95	6.13	7.93			
Average	8.37	6.57	8.47	7.99	6.21	8.09	8.02	6.57	7.91
Hemlock leather extract plus 8 per cent. dextrose	8.65	6.85	8.59	8.25	6.48	8.20	8.05-7.88	6.88-6.10	8.04-7.60
	8.74	6.67	8.45	8.34	6.31	8.06			
Average	8.69	6.76	8.52	8.29	6.39	8.13	7.91	6.47	7.80

[1] Blanks on the leather extracts have been deducted in all cases.

[2] Omitting one result which varied widely from all of the others.

Digitized by Google

TABLE II.—THE EFFECT OF VARIOUS PROCEDURES ON THE DETERMINATION OF REDUCING SUGARS IN A HEMLOCK LEATHER EXTRACT.[1]

Experiment No.	Method of sugar determination used	Blank on original leather extract			Leather extract plus 8 per cent. dextrose			Per cent. sugar in blank	Per cent. dextrose added	Per cent. total sugar present	Per cent. (+) or (−) error
		mg. cuprous oxide	Sugar calculated as dextrose		mg. cuprous oxide	Sugar calculated as dextrose					
			Per ct.	Av. per ct.		Per ct.	Av. per ct.				
1	Von Schroeder method: 200 cc. of extract cleared with 25 cc. saturated solution of Horn's basic lead acetate; lead removed by sodium sulphate; no magnesium sulphate was added; volume relations, $\left(\frac{180}{225} \times \frac{150}{200} \times \frac{1}{4} \times 3 = 0.45 \text{ gram.}\right)$ Reduction 30 minutes in boiling water bath.	14 8	1.22	1.22	88.1 86.7	7.97 7.80	7.88	1.22	8.00	9.22	−1.34
2	Von Schroeder method; treated the same as No. 1, except that 5 per cent. magnesium sulphate was present in the extract.	19.8 23.0	1.64 1.89	1.77	91.1 91.5 89 5	8.25 8.29 8.16	8.23	1.77	8.00	9.77	−1.54
3	Von Schroeder method; treated as in No. 1, except that fresh basic lead acetate prepared according to Von Schroeder was used for clarification.	10.0 8.7	0.80 0.70	0.75	85.3 87.2	7.66 7.85	7.75	0.75	8.00	8.75	−1.00
4	Von Schroeder method; treated as in No. 3, except that the hydrochloric acid used for inversion was neutralized by anhydrous sodium carbonate instead of sodium hydroxid solution.	(Using blank from No. 3)		0.75	87.5 85.6	7.89 7.69	7.79	0.75	8.00	8.75	−0.96

Digitized by Google

TABLE II.—(*Continued.*)

5	Munson-Walker method (modified); 200 cc. of extract cleared with 25 cc. saturated solution of Horn's basic lead acetate and the lead removed by sodium sulphate; volume relations, $\left(\frac{180}{225} \times \frac{150}{200} \times \frac{1}{4} \times 3 = 0.45 \text{ gram}\right)$. No magnesium sulphate was added.	06.1 05.7	0.59 0.54	0.57	80.8 81.0	7.73 7.75	7.74	0.57	8.00	8.57	−0.83
6	Munson-Walker method (modified); treated as in No. 5, except that 5 per cent. magnesium sulphate was present in the extract.	07.6 07.7	0.73 0.74	0.74	85.0 84.5	8.15 8.11	8.13	0.74	8.00	8.74	−0.61
7	Munson-Walker method (regular); 200 cc. extract plus 25 cc. normal lead acetate, lead removed by solid potassium oxalate; volume relations, $\left(\frac{150}{225} \times \frac{1}{4} \times 3 = \frac{1}{2} \text{ or } 0.5 \text{ gram}\right)$. No magnesium sulphate added.	(Using average blank of the A. L. C. A. Committee, 1912)		1.09	104.4 105.2	9.06 9.12	9.09	1.09	8.00	9.09	±0.00
8	Munson-Walker method (regular); treated as in No. 7, except that 5 per cent. magnesium sulphate was present in the extract.	16.7 15.1	1.43 1.28	1.36	108.4 106.1 106.1 107.6	9.42 9.18 9.18 9.34	9.28	1.36	8.00	9.36	−0.08
9	Munson-Walker method (modified); treated the same as No. 6, except that the lead was removed by potassium oxalate instead of with sodium sulphate.	06.5 08.4	0.56 0.71	0.64	84.3 85.9	7.28 7.41	7.35	0.64	8.00	8.64	−1.29

[1] This leather was Sample No. 2 in the A. L. C. A committee work on leather analysis, 1912.

Digitized by Google

potassium oxalate, no further work was carried out by this procedure.

The results of these experiments as shown in Table II, indicate that the low results obtained are not due to the joint use of basic lead acetate as clarifier and potassium oxalate as precipitant, since results equally low are obtained when the excess lead is removed by precipitation with sodium sulphate.

The causes of the inaccurate results obtained when basic lead acetate is used in clarifying leather extracts.—A hemlock leather extract was prepared (15 g. per liter) and labeled solution No. 1. To one-half of this extract was added 8 per cent. of dextrose on the basis of the leather and this was labeled solution No. 2. A few drops of toluol were added to both solutions to prevent fermentation. These solutions were then analyzed by the A. L. C. A. method (using 25 cc. of normal lead acetate to 200 cc. of leather extract) and by the Von Schroeder method (using 20 cc. of basic lead acetate to 200 cc. of leather extract and obtaining the dextrose from the weighed Cu_2O by calculating the weighed Cu_2O to Cu, and the Cu to dextrose using the Table of Koch and Ruhsam). The results obtained are shown in Table III.

We are indebted to Dr. Paessler, who co-operated with us in this work and who kindly prepared solutions No. 3 and No. 4, at our request, in a manner similar to that used for solutions No. 1 and No. 2. The amount of added dextrose in solution No. 4 was not known by the analyst at the time the analyses were made. Table No. 4 contains the results of the analyses of these solutions. They indicate that 10 per cent. of dextrose on the basis of the leather was added to solution No. 4.

In order to prove that it is permissible to calculate the Copper from the Cu_2O without introducing an appreciable error, we dissolved the Cu_2O in HNO_3 and then determined the copper volumetrically by the LOW method (*Jour. Amer. Chem. Soc.*, 1902, 24, 1082). The results given in the second part of Table IV show that no appreciable error is introduced.

Noting that the minus error obtained in the experiments shown in Table III by the Von Schroeder method using 20 cc. of basic lead acetate to 200 cc. of leather extract was not so great as that obtained in experiment No. 4, Table II, where 25 cc. of basic lead

Digitized by Google

acetate were used; and bearing in mind the known fact that excessive amounts of basic lead acetate remove sugars present,[10] it was planned to study the effect of varying the amounts of basic lead acetate, to determine whether or not too much was being used.

TABLE III.—DEXTROSE DETERMINATIONS IN LEATHER EXTRACTS.
SOLUTIONS NO. 1 AND NO. 2.
American Leather Chemists' Association's Method.

Per cent. of dextrose calculated from weight of Cu_2O						
Solution No. 1 Without dextrose added			Solution No. 2 With dextrose added			Per cent. added dextrose found
mg. Cu_2O	Per cent. dextrose	Average per cent. dextrose	mg. Cu_2O	Per cent. dextrose	Average per cent. dextrose	
(A)			(A)			
10.2	0.82		101.3	8.78		
9.6	0.77		102.2	8.85		
(B)			(B)			
9.8	0.78		102.2	8.86		
10.5	0.85		100.3	8.69		
		0.805			8.795	7.99

Von Schroeder Method (Using 20 cc. basic lead acetate to 200 cc. of extract.)

Per cent. of dextrose calculated from weight of Cu_2O.						
Solution No. 1 Without dextrose added			Solution No. 2 With dextrose added			Per cent. added dextrose found
mg. Cu_2O	Per cent. dextrose	Average per cent. dextrose	mg. Cu_2O	Per cent. dextrose	Average per cent. dextrose	
(A)			(A)			
4.2	0.31		87.5	7.58		
9.4	0.73		90.9	7.90		
			90.9	7.90		
(B)			(B)			
7.1	0.55		89.4	7.77		
7.7	0.60		88.9	7.72		
			91.7	7.98		
		0.547			7.808	7.260

(A) = First clarification. (B) = Second clarification.

[10] *Jour. Soc. Chem. Ind.*, Vol. 27, p. 53; Vol. 28, p. 729; and Handbook on Sugar Analysis, by C. A. Brown, p. 215. (John Wiley and Sons, New York.)

Digitized by Google

TABLE IV.—SOLUTIONS NO. 3 AND 4.

American Leather Chemists' Association's Method. Per cent. dextrose calculated from weight of Cu_2O							Procedure of Von Schroeder (using 5 cc. basic lead acetate to 200 cc. leather extract.) Per cent. dextrose calculated from weight of Cu_2O						
Solution No. 3 Without dextrose added			Solution No. 4 With dextrose added			Per cent. added dextrose found	Solution No. 3 Without dextrose added			Solution No. 4 With dextrose added			Per cent. added dextrose found
mg. Cu_2O	Per cent. dextrose	Average per cent. dextrose	mg. Cu_2O	Per cent. dextrose	Average per cent. dextrose		mg. Cu_2O	Per cent. dextrose	Average per cent. dextrose	mg. Cu_2O	Per cent. dextrose	Average per cent. dextrose	
(A)			(A)				(A)			(A)			
7.0	0.54		119.6	10.43			6.7	0.69		89.9	10.29		
6.5	0.50		121.2	10.56			7.7	0.79		90.7	10.40		
			121.3	10.57						89.4	10.23		
(B)			(B)				(B)			(B)			
7.0	0.54		121.2	10.56			9.9	1.02		91.5	10.50		
7.3	0.57		120.7	10.52			9.8	1.01		91.3	10.47		
		0.537	121.2	10.56	10.533	9.996			0.877	90.2	10.33	10.37	9.493

Percentages of dextrose calculated from Cu obtained from Cu_2O by titration.

mg. Cu	Per cent. dextrose	Average per cent. dextrose	mg. Cu	Per cent. dextrose	Average per cent. dextrose	Per cent. added dextrose found	mg. Cu	Per cent. dextrose	Average per cent. dextrose	mg. Cu	Per cent. dextrose	Average per cent. dextrose	Per cent. added dextrose found
(A)			(A)				(A)			(A)			
5.7	0.49		105.5	10.34			6.1	0.71		78.3	10.21		
5.8	0.50		107.0	10.50			5.3	0.57		Lost	—		
			107.0	10.50						77.6	10.11		
(B)			(B)				(B)			(B)			
6.3	0.54		107.5	10.54			7.8	0.90		79.5	10.39		
6.1	0.52		107.0	10.50			7.3	0.84		79.6	10.39		
		0.512	107.0	10.50	10.48	9 968			0.755	78.6	10.25	10.27	9.515

(A) = First clarification. (B) = Second clarification.

Digitized by Google

At that time Dr. Paessler[11] called our attention to the fact that we were using a much greater excess of basic lead acetate than the Von Schroeder method called for. The above facts together with a careful examination of the procedures prescribed by different leather chemists (see Table V) led us to believe that the use of the excessive amounts of basic lead acetate was the real cause of the low results obtained.

TABLE V.—VARYING AMOUNTS OF BASIC LEAD ACETATE USED IN CLARIFYING LEATHER EXTRACTS.

Name	Grams of leather per liter	Cc. of leather extract used	Cc. of lead subacetate used	Equivalent grams of leather to 20 cc. of lead subacetate
Von Schroeder[1] (1898)	20	400	10	16.0
Former A. L. C. A. Method[2] (1908)	15	500	20	7.5
F. P. Veitch[3] (1908)	10	500	25	4.0
J. G. Parker[4] (1908)	15	200	20	3.0
H. R. Procter[5] (1908)	25	400	20	10.0
Hans Sichling[6] (1910)	20	400	10	16.0
H. G. Bennett[7] (1910)	50	200	20	10.0
L. Jacomet[8] (1911)	20	400	10	16.0
Paessler[9] (1914)	15	200	5	12.0
F. P. Veitch[10] (1912)	15	200	25	2.4

[1] Von Schroeder and Bartel, *Ding. Poly. J.*, 1898, Vol. 293, p. 253.
[2] JOURNAL American Leather Chemists' Association, Vol. 3, p. 8.
[3] JOURNAL American Leather Chemists' Association, Vol. 3, p. 261.
[4] JOURNAL American Leather Chemists, Association, Vol. 3, p. 262.
[5] Leather Industries' Laboratory Book, p. 270, and Leather Chemists' Pocket Book, 1912, p. 171.
[6] *Collegium*, 1910, p. 327
[7] The Manufacture of Leather, p. 402.
[8] Matieres Tannantes Cuirs, p. 85.
[9] Paessler, according to the procedure sent to the Leather and Paper Laboratory for co-operative work in 1914.
[10] Procedure as sent out by the Leather and Paper Laboratory, 1912.

To secure definite information on this point, determinations of dextrose were then made on the original hemlock leather extract and on the same extract with 8 per cent. of dextrose added, following the Von Schroeder method, but using 4, 6, and 10 cc. respectively of basic lead acetate with 200 cc. portions of the two extracts. The results of these experiments are given below in Table VI.

[11] Private communication in which he suggested the use of 5 cc. of basic lead acetate to 200 cc. of leather extract (15 g. per liter), after having experimented and found that larger amounts of basic lead acetate removed sugar present in a pure dextrose solution.

Digitized by Google

TABLE VI.—EFFECT OF VARYING THE AMOUNT OF BASIC LEAD ACETATE USED.

Cc. basic lead acetate used per 200 cc. leather extract	Solution A No dextrose added		Solution B With 8 per cent. of dextrose added		Per cent. of added dextrose found
	Per cent.	Average per cent.	Per cent.	Average per cent.	
4 cc.....	1.04		9.20		
	1.20		9.38		
	0.94	1.06		9.29	8.23
6 cc.....	0.88		8.96		
	0.81		8.71		
	0.77	0.82		8.83	8.01
10 cc.....	0.59		8.39		
	0.50	0.54	8.49	8.44	7.90

From these results it appears that on this *leather extract* 4 cc. of basic lead acetate is not sufficient to precipitate all of the tannins and non-tannins, while with 6 cc. all copper reducing bodies other than dextrose are removed and with 10cc. of basic lead acetate apparently some of the dextrose normally present in the extract is removed, and there is a tendency to low results even on the added dextrose. In both of these cases, however, results close to the theoretical for total added sugar are obtained, after deducting the respective blanks, while in the case where 4 cc. of basic lead acetate was used the results are slightly higher. On an extract from the same leather 7.26 per cent. dextrose was found, using 20 cc. of basic lead acetate to 200 cc. of extract. Thus we might assume that 15 cc. of basic lead acetate would give about 7.6 per cent. of dextrose. This would give a limit of from 6 to 10 cc. of basic lead acetate for 3 g. of this leather. This relation might and probably would be different with each leather analyzed, and thus it would always be necessary to determine approximately the correct amount of lead acetate required to clarify properly the solution. It is evident that this would involve additional work and loss of time.

Sufficient data have already been obtained to prove beyond doubt that the use of a large excess of basic lead acetate as clarifier for leather extracts will remove dextrose actually added. Since the excess of basic lead acetate used must be confined within narrow limits, the question at once arises as to whether 5 cc. of basic lead acetate will be sufficient to clarify extracts in

Digitized by Google

which the soluble solids, other than dextrose, are higher than those present in the leathers already examined. To determine this point the following experiments were planned:

Four leathers were chosen from analyzed laboratory samples, in which the soluble solids other than dextrose and epsom salts varied from 13 to 30 per cent., it having been found that these represented the maximum and minimum percentages of soluble solids other than dextrose and epsom salts in over 100 analyzed leathers. Two liters of extract (15 g. per liter) from each of these leathers were prepared, and to one liter portions of each of these extracts were added 8 per cent. of dextrose on the basis of the leather.

The eight extracts used in these experiments were as follows:

No. 1 Leather extract containing 13.5% of soluble solids.
No. 2 " " " 16.8% " " "
No. 3 " " " 24.0% " " "
No. 4 " " " 30.0% " " "
No. 5 " " " 13.5% " " " plus 8% dextrose.
No. 6 " " " 16.8% " " " " 8% "
No. 7 " " " 24.0% " " " " 8% "
No. 8 " " " 30.0% " " " " 8% "

Dextrose was determined on 200 cc. portions of each of these eight extracts by (A) the A. L. C. A. method, (1) using 25 cc. of normal lead acetate, (2) using 30 cc. of normal lead acetate; (B) the Von Schroeder method, (1) using 5 cc. of basic lead acetate, (2) using 6 cc. of basic lead acetate. The results of these experiments are given in Table No. 7.

These experiments show: (1) That the A. L. C. A. method using 25 cc. of a saturated solution of normal lead acetate gives excellent results even when applied to leathers in which the soluble solids vary from 13 to 30 per cent. (2) That an increase of the amount of normal lead acetate used does not materially affect the results obtained by this method; and indicates that 25 cc. of normal lead acetate are sufficient for the leathers of the highest soluble solid content. (3) That the Von Schroeder method, using 5 cc. of basic lead acetate to 200 cc. of the leather extract, can be safely applied only to the first two leathers of this series in which the soluble solids vary from 13 to 16.8 per cent.

Digitized by Google

TABLE VII.—CLARIFICATION OF EXTRACTS OF LEATHER CONTAINING VARYING AMOUNTS OF SOLUBLE SOLIDS.

	A. L. C. A. Official Method, 1914. (Varying normal lead acetate.)						Von Schroeder Method. (Varying basic lead acetate.)					
	25 cc. of normal lead acetate			30 cc. of normal lead acetate			5 cc. of basic lead acetate			6 cc. of basic lead acetate		
Extract No.	Per cent. dextrose	Average per cent. dextrose	Per cent. added dextrose found	Per cent. dextrose	Average per cent. dextrose	Per cent. added dextrose found	Per cent. dextrose	Average per cent. dextrose	Per cent. added dextrose found	Per cent. dextrose	Average per cent. dextrose	Per cent. added dextrose found
1	0.18			0.20			0.21			0.64		
	0.12	0.15		0.05	0.13		0.27	0.24		0.38	0.51	
2	0.34			0.23			0.84			0.41		
	0.25	0.29		0.20	0.22		0.54	0.69		0.71	0.56	
3	2.67			2.72			4.19			4.03		
	2.69	2.68		2.64	2.68		4.05	4.12		3.98	4.00	
4	3.10			2.98			5.09			4.49		
	3.09	3.09		2.90	2.94		5.14	5.12		4.54	4.47	
5	8.32			8.30			8.42			8.64		
	8.30	8.31	8.16	8.32	8.31	8.18	8.48	8.45	8.21	8.62	8.63	8.12
6	8.27			8.40			8.73			8.38		
	8.32	8.29	8.00	8.33	8.37	8.15	8.69	8.71	8.02	8.31	8.35	7.79
7	10.83			10.64			12.78			12.19		
	10.62	10.72	8.04	10.54	10.59	7.91	13.22	13.00	8.88	12.29	12.24	8.24
8	11.23			11.03			13.62			13.66		
	11.08	11.15	8.06	10.90	10.96	8.02	13.67	13.65	8.53	13.23	13.44	8.97

Digitized by Google

The data in Table VIII show the effect, upon the results obtained by the A. L. C. A. method, of varying the amount of normal lead acetate used with 200 cc. of leather extract. The leather used contained about 16 per cent. of soluble solids. (15 g. of leather per liter.)

TABLE VIII.—AMERICAN LEATHER CHEMISTS' ASSOCIATION METHOD VARYING THE AMOUNT OF NORMAL LEAD ACETATE USED.

Leather extract without added dextrose.

Volume of normal lead acetate used	Percentage of dextrose found	Average percent. of dextrose found	Percentage of added dextrose found
5 cc	1.75		
	1.82	1.79	
10 cc	1.29		
	1.35	1.32	
15 cc	0.91		
	0.97	0.94	
20 cc	0.86		
	0.78	0.82	
25 cc	0.77		
	0.74	0.76	
30 cc	0.77		
	0.63	0.70	
35 cc	0.78		
	0.75	0.76	
Leather extract with 8 per cent. of dextrose added.			
20 cc	8.79		
	8.75	8.77	7.95
35 cc	8.59		
	8.63	8.61	7.85

The cause of our low results by the Von Schroeder method has been definitely shown. Too large a quantity of basic lead acetate was used. It is possible to obtain good results by the Von Schroeder procedure using basic lead acetate. The facts still remain, however, (1) that when basic lead acetate is used in too great excess low results are obtained and (2) when an insufficient amount of basic lead acetate is used too high results are obtained. In other words the analyst must know, prior to the analysis, to within small limits the amount of lead precipitable constituents present in the leather extract in order to add

Digitized by Google

the proper amount of basic lead acetate. An amount must be chosen which will be sufficient to remove all of the copper reducing bodies without removing any dextrose. Thus prior to the determination of sugar the chemist must know the amount of soluble matter other than dextrose in the *leather extract under examination;* and then either accommodate the amount of basic lead acetate used to the amount of soluble solids present, or he must dilute or concentrate the leather extract until the amount of soluble matter bears the proper proportion to the amount of lead acetate. The percentage of total soluble solids will not give a correct value from which to decide upon the proper amount of basic lead acetate to be used, since the percentage of total soluble solids will include the unknown amount of dextrose present.

An examination of the foregoing results will show that the A. L. C. A. method using 25 cc. of normal lead acetate does not give low results even when the soluble solids are very low, or high results when the soluble solids are extremely high. This cannot be said of the Von Schroeder method using either 5 cc. or 6 cc. of basic lead acetate.

CONCLUSIONS.

1. The joint use of basic lead acetate as clarifier for leather extracts and potassium oxalate as precipitant for the excess of lead was not the cause of the low results obtained by the A. L. C. A. committee on leather analysis for 1912.

2. The low results obtained in that work were due to the use of too large an excess of basic lead acetate.

3. The Von Schroeder procedure, using 5 cc. of basic lead acetate to 200 cc. of the leather extract is far superior to the use of 20 cc. of basic lead acetate to 200 cc. of the leather extract and can be safely used for *some leathers.*

4. Before using basic lead acetate for clarification of leather extracts, it must be learned for each leather examined, first, that the soluble solid content, other than dextrose, is not so low as to render the excess of basic lead acetate sufficiently great to remove dextrose; and secondly, that the soluble solid content other than dextrose is not too great to be removed by the amount of basic lead acetate used.

Digitized by Google

5. The use of basic lead acetate without first determining the proper proportion required for the extract *under examination* is liable to introduce an error, and if the proper proportions are determined, causes much inconvenience and loss of time.

6. The differences in the results reported by Paessler and those obtained by the A. L. C. A. committee on leather analysis for 1912 were due to the fact that Paessler used the "Allihn" table for the calculation of his results instead of the "Munson and Walker" table which the prescribed method called for.

7. The reliability of the A. L. C. A. method has been clearly shown; (1) by its closely agreeing duplicates, (2) by the fact that theoretical percentages of dextrose were found, (3) by the fact that theoretical results were obtained in extracts of leathers in which the soluble solids varied from 13 to 30 per cent., and (4) by the fact that the results are not seriously affected by use of a considerable excess of normal lead acetate.

The general conclusions to be drawn from all of the foregoing experiments are: (1) that the A. L. C. A. method for clarification of leather extracts using 25 cc. of a saturated solution of normal lead acetate proves very satisfactory for practically all leather extracts, and (2) that by the Von Schroeder method in experienced hands, and with *great precaution in regard to the ratio between the amount of basic lead acetate used and the amount of soluble solids present* fairly good results may be obtained *if the soluble solid content other than dextrose and epsom salts is known or can be easily determined.*

SOME NEW TESTS FOR TANNING MATERIALS.*

By Hugh Garner Bennett, M. Sc., F. C. S.

The Cobalt Test.—Whilst examining the properties of the different tannates of cobalt, the writer observed that these compounds yielded typical colors when allowed to react with hydrogen peroxide. After some experimenting the best conditions for observing these were discovered. The reagents required are:

1. A very dilute infusion of the tanning material under examination, containing roughly about 0.1 per cent. of tannin.

* *Shoe and Leather Reporter*, September 17, 1914.

Digitized by Google

2. Hydrogen peroxide of about "16 vols." strength approximately.

3. A solution containing 1 per cent. cobalt nitrate and 10 per cent. ammonium carbonate. This last reagent is best made by dissolving 25 grams ammonium carbonate in a 250 cc. flask in about 150 cc. of distilled water, and then adding slowly 2.5 grams cobalt nitrate previously dissolved in a little distilled water.

The actual test is carried out as follows: 6 or 7 cc. tanning infusion (which need not be filtered) is poured in a test tube with an equal volume of peroxide, and 3 or 4 drops of cobalt solution are added cautiously drop by drop.

The writer has carried out this test with nine of the most commonly employed tanning materials, and has found them to behave towards this reagent in one of three ways.

Class 1 embracing valonia, chestnut extract and oakwood extract, develops a purple coloration. If a brown is obtained the tannin infusion is too strong.

Class 2, which includes sumac (Sicilian), myrobalans and algarobilla, show an orange color. Gallotannic acid and gallic acids also give this orange color which may be regarded as another test for gallic acid. It sometimes happens (especially with myrobalans) that the first drop of cobalt solution shows a very transient purple tinge, but subsequent drops of the reagent show the color characteristic of the class.

Class 3. In these cases a bright red color immediately develops quite distinct from the preceding classes. This class embraces quebracho, mimosa bark and gambier.

Tanning materials can be divided into two classes named the "catechol tannins" and the "pyrogallol tannins," on account of the fact that on dry distillation they yield catechol and pyrogallol respectively. This division is also in harmony with many other tests, such as the bromine water test. It will be noticed by those familiar with this scientific classification, that the materials in Class 3 above all are known as catechol tans, whilst those in Classes 1 and 2 are all belonging to the pyrogallol class. It is clear, therefore, that this cobalt test provides a means for subdividing the pyrogallol division of tanning materials.

Some years ago the writer published in the *Shoe and Leather*

Digitized by Google

Reporter a test he had devised for the same purpose, viz., the chromate test. It may be as well to describe this briefly. A tanning infusion (0.4 per cent. tannin) is diluted with an equal volume of sodium bisulphite and 1 or 2 drops of a 10 per cent. potassium chromate solution are added. In this case also characteristic results are obtained and it is interesting to note that the sub-division there proposed of the pyrogallol tannins, corresponds exactly with the sub-division effected by the cobalt test being described. Class 1 materials give a deep purple with the chromate test and Class 2 materials a transient blood red, which is also given by gallic acid. The two tests may therefore be regarded as confirmatory of one another and of this sub-division.

Previously published tests of various other workers are also in harmony with this arrangement and it will not be out of place to mention one or two of these as they are very simple to execute. It may be understood that all may be carried out with tanning material infusions containing about 0.4 per cent. tannin.

1. A few drops of this infusion are placed in contact with a crystal of sodium sulphite on a white tile or in a porcelain basin. Class 1 develop a bright purplish pink, whilst Class 2 do not give this reaction.

2. A small quantity of tannin infusion is placed in a porcelain basin and an excess of lime water added. A yellow precipitate is in each case obtained first, which quickly changes into a red purple for Class 1 materials and into a green for Class 2 materials.

3. To a small quantity of the infusion a little of a 1 per cent. copper sulphate solution is added, followed by excess of ammonia. In each case a dark precipitate is obtained, but the materials of Class 1 show it with a distinct reddish tinge.

4. To 5 cc. tannin infusion add 10 cc. 10 per cent. acetic acid and 5 cc. 10 per cent. lead acetate solution. After mixing and filtering, add a little of a 1 per cent. iron alum solution. Class 1. show no color, having been completely precipitated, whilst Class 2 all show a blue-black color.

Taking the above facts into consideration and also the results of the tests to be described later, it would seem that this grouping of the pyrogallol materials is in very good agreement. In a recently published work of Prof. Procter, however, the formalde-

Digitized by Google

hyde test is chosen for distinguishing the groups. This seems very unfortunate, as this happens to be the only test which is in disagreement with all the rest mentioned above and below. The difference is that the formalin test places myrobalans in Class 1. This, however, is not only in disagreement with the other tests but also with the practical experience of tanners, who would mostly consider myrobalans as akin to algarobilla and sumac.

It is difficult to say to what the colors of the cobalt test are really due, but there are one or two points which should be noted. There is in the first place some little resemblance to the chromate test. The colors produced are somewhat alike, both for Classes 1 and 2. They both involve the use of strong oxidizing agents (peroxide and chromate) and they both involve the use of metals which usually give colored salts and compounds. In the cobalt test there is little doubt that the active reagent is ammonium cobaltate $[(NH_4)_2 CoO_4]$ known to be formed by the oxidation of cobalt salts by peroxide in alkaline solution. Indeed, this green compound may be prepared first and the tanning infusion added to it. This cobaltate is then strictly analogous with the chromates. That this is the case is also shown by the fact that solutions of nickel salts (which do not form nickelates) will not give this test. It is the writer's intention to examine later the manganates and ferrates to see if they will supply analogous results. There are, however, some points of essential difference between the two tests, one being that the chromate test is in acid solution and sulphurous acid is essential to its success, whereas sulphurous acid bleaches at once the colors of the cobaltate test, which is carried out in alkaline solution. Another difference is that the typical catechols tannins (Class 3) give no reaction at all with the chromate test. Mimosa bark, however is an exception amongst the catechols.

The Iodine Test.—Some time ago a test was published [O. Schewket, *Biochem. Zeits.*, 1913, 52, 271-274] for gallotannic and gallic acids, which was said to distinguish them from the tannins of "kino" "catechu" and "cinchona." The test consists in adding a very little weak tannin infusion to a large flask and diluting largely with hard water (400-500 cc.), and then adding about 2 cc. of a 1 per cent. solution of iodine in potassium iodide.

Digitized by Google

Schewket reports a red-violet color as indicating gallic or gallotannic acid.

The writer has been applying this test to the commercial tanning materials with striking results, and has found that many of the different tannery materials yield characteristic colors, whilst some yield no color at all. Moreover the color obtained with gallic and gallotannic acids appear to the writer more red than violet. The function of the hard water is to provide a mild alkali. If hard water is not available very weak solutions of sodium carbonate, phosphate, borate, acetate, etc., may be employed. The writer uses tap water which contains about 23 parts chalk per 100,000. This is mentioned as the color shade might conceivably be influenced by the nature and concentration of this alkali.

It is surprising how dilute the tan liquor may be made and yet answer this test; indeed if any trouble is experienced with it, it is probably because the solution is not dilute enough, for it is necessary to have the iodine in excess.

The tanning materials when arranged according to this test fall into the same groups as with the chromate test and further confirm that arrangement.

1. Valonia, chestnut extract, and oakwood extract yield a dark blue color.

2. Myrobalans, sumac, algarobilla, mimosa bark, gallotannic and gallic acids yield a purple-red color.

3. Quebracho and gambier yield no color at all. It will be noticed that although mimosa bark is undoubtedly a catechol tannin (yielding a bromine water precipitate, reds, etc.) it appears to behave in some respects like a pyrogallol tannin, *e. g.*, chromate test, iodine test, and iron test. As each of these is a test for gallic acid it would appear that mimosa bark either contains gallic acid free or a gallic acid grouping in its molecule. Proctor classes it amongst "mixed and doubtful" but my own experience with the material indicates that the tannin is one chemical individual rather than a mixture. There seems no reason why a section of the catechol tans should not contain a pyrogallol grouping also.

In the reaction also the nature of the colors is obscure, and is likely to remain so for some time, as they can only be produced

Digitized by Google

in such small quantities. We may note, however, that the reagent is again an oxidizing agent, and there is some resemblance to the cobalt test in the respect that the test works in the presence of a weak alkali. In harmony with the theory the writer has experimented with other oxidizing agents and weak alkalies and has found that analogous results may sometimes be obtained, *e. g.*, (1) hard water and a little bromine water, but the color is easily bleached by excess of bromine; (2) hydrogen peroxide and potassium cyanide.

Ferricyanide Tests.—It has long been known that potassium ferricyanide in ammoniacal solution gives a color reaction with tannin. This is one of the "general" reactions of tannins. A crystal of ferricyanide dissolved in a little 10 per cent. ammonia makes a convenient reagent.

If, however, the test be carried out in a similar manner to the iodine test described above, different colors are obtained which classify the tanning materials almost as before. A little tannin infusion is largely diluted with hard water, and a little ammoniacal ferricyanide is added. The colors are as follows:

1. Valonia and chestnut and oakwood extracts yield a purple color.

2. Myrobalans, algarobilla and sumac yield a dark orange. The first of these three sometimes shows a very transient trace of purple.

3. Quebracho, mimosa bark, gambier, gallotannic and gallic acids show a bright orange color.

It is probable that sections 2 and 3 of this test would be better classed together for the exact orange shade may be influenced by other factors.

Another way of employing ferricyanide is to dispense with the ammonia. If the test be carried out similarly in other respects, Class 1 yield the purple color as usual, but the other materials do not react. This supplies further evidence of the close similarity of the Class 1 materials and also of the theory that the essentials are to have a weak alkali and an oxidizing agent, in this case the ferricyanide.

It is of interest to note also that here again we have a metal involved (iron) which yields colored compounds, but the iodine

Digitized by Google

and bromine tests make it doubtful how far this is essential. On the whole, the explanation of these colors is probably that the tannins are in a state of higher oxidation, what may be called "per-tannic" acids, or "pertannates" being formed; these, however, are very unstable and only formed under special conditions.

Sodium Arsenate Test.—In conclusion of this article, it may be of interest to note another test which the writer has found, recently to distinguish the pyrogallol from the catechol materials. It is known that a solution of sodium arsenate gives with gallic and gallotannic acid solutions a deep blue green color when the mixture is allowed to stand in air from which it absorbs oxygen.

The writer has found that if tannin infusions are diluted until they no longer color the water very distinctly, sodium arsenate then added, and the mixture allowed to stand an hour or two, all the pyrogallol tans develop a green color.

The "Class 1" materials (see above) all show a dark green, perhaps on account of their darker color.

Myrobalans, sumac and algarobilla yield a yellow green—no doubt because of the yellow dyestuff which each of these materials contains. The catechol tannins, on the other hand, develop a bright red color. This, therefore, is yet another test for distinguishing the two principal groups of tanning materials. It is the writer's intention to examine shortly the catechol tannins in more detail, and if any interesting results are obtained, perhaps it may be possible to communicate them to the *Shoe and Leather Reporter* at a future date.

A NEW FORM OF EVAPORATOR AND DRYER.

By L. Balderston.

Before describing the modified form of apparatus which is the subject of this note, it may not be amiss to review the conditions which a satisfactory evaporator and dryer should fulfill. The plate on which the dishes are set must be horizontal, and of heavy enough material not to sag in the middle with use, in order that the film of material left in the bottom on evaporation may be of uniform thickness and so dry evenly. The cover must fit neatly so that there will be as little flow of air as possible along

Digitized by Google

the plate on which the dishes rest, as this would prevent those near the edge from reaching the desired temperature. There must be a sufficient but not too large flow of air through the confined space, in order that the water of evaporation may be carried off without cooling the interior below 95 or 97 degrees C. This air supply must enter all around the walls at a height above the base plate a little greater than the height of the dishes and pass out at the top. There must be a free flow of steam through the double-walled cover, giving in the neighborhood of one gallon of water of condensation per hour from an apparatus 30 inches square. The constant level apparatus, which should be not less than two inches in diameter, should communicate with the boiler near the bottom, and be adjusted so as to keep about 4 inches of water in a boiler 6 inches deep. The cover should be so arranged as to be easily raised without disturbing any connections. The apparatus should be of copper throughout. If the joints are made by soldering, they will inevitably become leaky after prolonged use, as the solder corrodes under the continued attack of steam, when in contact with copper. The seams should therefore be brazed together. The construction of the cover should be as simple as is consistent with efficiency, so as to save expense. The flow of steam from the boiler to the cover is usually provided for by two tapered ground joints of brass with about 1 inch opening, one on each side. These joints do not need to be very perfect, as the film of water which forms in them between the brass surfaces suffices in the absence of pressure to make a good seal.

It is customary to connect the apparatus with a condenser so that it may furnish a supply of distilled water. Where a number of "ovens" are used in one laboratory, it is convenient to have them connected to one condenser, instead of putting a condenser for each on the cover. In the form of oven commonly used, the steam escapes from the cover at the top, the cover being shaped like a pyramid. Where several are connected to one condenser, it is necessary to disconnect the steam escape in order to lift the cover, or else to use some sort of more or less complicated flexible pipe for the steam. Where each oven has its condenser fastened to its cover, the weight to be lifted is

Digitized by Google

considerable, and rubber hose connections are necessary for the water to and from the condenser, requiring to be looked after quite frequently.

In this laboratory eight ovens are in use, and the matter of leaks above referred to is a constant source of annoyance. The hinges by which the covers are attached are also held with solder, and they often come loose. Beside, the disconnecting and connecting of the steam escape is troublesome.

As W. K. Alsop and I went over the matter of possible improvements, it occurred to us that there is no necessity to take the steam out at the top. The ordinary form of steam radiator for heating purposes has but one opening, at which the steam enters and the water of condensation escapes. We decided to try taking the steam out at the hinge. It might seem that in such a case not all parts of the cover would be heated equally. We reasoned that if there is an abundant steam supply, if any part of the cover tended to become cool, condensation there would make a partial vacuum, and more steam would flow to that spot. An old oven was accordingly fitted up as follows: the hinges were taken off and replaced by a piece of inch brass pipe extending all the way across the back at the bottom and projecting several inches at each end. Openings from the inside of the hollow cover into this pipe were provided, so that the escape of the steam and water of condensation could take place through the pipe, which is sealed at one end, and connects at the other with a suitable condenser. The projecting ends of the pipe rest in supports fastened to the boiler, so that the pipe acts as a hinge, and as the joint connecting it with the condenser is loose, the cover may be raised without disturbing anything. The arrangement works perfectly, the space inside being heated quite as fully and uniformly as in the other ovens from which the steam escapes at the top.

The next point which claimed attention was the matter of reducing cost by simplifying the shape of the cover. Since the steam was not to escape at the top, a pyramidal shape was not necessary, and if the roof of the cover were close enough to the dishes, the whole enclosed space could be kept hot without making the side walls double. To test this reasoning, a cover was

Digitized by Google

made whose roof has a double slope like that of an ordinary house, rising 4 inches from edge to ridge on an oven 24 inches wide. The gable ends and front edge are of one thickness of metal, the back vertical wall being double as usual, to provide connection with the pipe hinge. Steam enters at each end of the top angle of the roof. The water of condensation from the front slope of the roof flows through a small pipe at the side to the bottom of the back. In the oven room of this laboratory, where the temperature during the night is about 110 degrees F. this arrangement works very well. We think, however, that it will be well to line the single walls with asbestos paper. We were fearful that the height of the roof being so small there would not be a sufficient draft created to make a good flow of air. Four pieces of inch pipe equally spaced along the ridge, opening out from the covered space and rising 8 inches above the top provide as much draft as the ordinary form of oven. The air inlets are larger and less numerous than usual, ½ inch in diameter and four on a side. It will be easily understood that this form of cover is very much simpler and less expensive to make than one which is double-walled throughout, and pyramidal in shape.

Laboratory of the Elk Tanning Company, Ridgway, Pa.

ABSTRACTS.

Tanning Extracts from Black Mangrove Bark. WM. F. DOTY, Consul, Nassau, Bahamas, in *Consular Reports.* Dr. Charles S. Dolley has experimented with the bark of black mangrove, (Avicenna nitida), and obtained an excellent extract. This mangrove is abundant in the Bahamas, especially on the largest Island, Andros.

Use of the so-called "ulmo" Bark. ANON. *Conceria*, **22**, 124. This bark is obtained from the "ulmo" tree (*Eucouptia cordifoglia*) and was first used for extraction of its tanning constituents by the "Compagnia Chitera de Estraccion de Tannino" located at Santiago. Extracts of this bark are now prepared. The tanning extract of quebracho surpasses "ulmo" extract in color, consistency and resistance to the action of light, but is somewhat inferior thereto in content of tanning substances.

H. S. PAINE.

Constitution of Tannin XI. A. GEAKE AND M. NIERENSTEIN. *Collegium,* 1914, 417-24. Nierenstein now abandons his earlier formula of

Digitized by Google

tannin as digalloyl-leukodigallic anhydride. Agreeing with Feist and with Fischer and Freudenberg, he now includes glucose in the molecule. This he had earlier overlooked, through employment of alkali for hydrolysis.

Following Fischer and Freudenberg, various tannin preparations from Schering, Kahlbaum, Merck and Schuchardt were hydrolyzed with dilute sulphuric acid for 70 hours; the results varied greatly, even with the same preparation, giving from 2.16 to 8.34 per cent. glucose determined by reduction with Fehling's solution (Bertrand). The filtrate gave varying colors with $FeCl_3$, KCN and NaOH. The results are considered only as qualitative proofs of glucose in the tannin molecule. A few tannin preparations were found to contain free glucose, but these were not used in the research work. Biddle and Kelley found that the rotation of tannin was lowered by addition of beer yeast and Nierenstein had regarded this as confirming the assumption that glucose was merely an impurity. On repeating these experiments himself, and avoiding all infection from mold, he finds no change in the rotation.

A partial hydrolysis of tannin (material from Schering) was experimented upon. This was heated on the water bath for 4 hours in 50 gram portions with 500 cc. of 5 per cent. H_2SO_4. From the product were fractionated: (1) 60-70 per cent. of an anhydrous substance analyzing like tannin, precipitating gelatine and being fixed quantitatively by casein. On continued hydrolysis it gave 8.7 per cent. glucose. It differed from tannin and from Fischer and Freudenberg's penta-acetylglucose in its higher rotation. It is improbable that it is unaltered tannin since considerable gallic acid (2) was formed, 20-25 per cent., and no free glucose. (3) A fine crystallizing, sugar-free substance, 2½-4 per cent., not yet identified.

W. J. K.

The Ox-warble Problem. SAMUEL FRASER. *Country Gentleman*, through *Hide and Leather*, Sept. 19. The author estimates the yearly damage from the warble in the United States at $50,000,000. From March till June the eggs are laid on the legs of cattle. It has been commonly supposed that the young maggots are licked off the legs and after thus being taken into the gullet migrate through the body until they find a lodgment just under the skin, remaining in this position for several months before they cut their way out, fall to the ground, burrow, and pass into the pupa condition. It has been observed that stock are not attacked when standing in the water, or in the shade, which furnishes an additional reason for providing water and shade in pastures. In Minnesota and Dakota the warble is virtually unknown. It was formerly advised that the backs of young cattle be smeared in order to prevent the laying of eggs. Although this would not be effective in the way intended, such applications may kill some of the grubs. One of the most effective cures is to squeeze out the grubs with the thumbs. Professor Curtice of the Rhode Island Station discovered as long ago as 1891 that the young grubs are found in the walls of the gullet and other parts of the body, travelling toward the back. Professor Carpenter, of the Irish Experiment Station,

Digitized by Google

covered the backs and sides of a number of animals during a whole season. They had as many warbles the following year as unprotected animals. This seems to disprove the old belief that the eggs are laid on the back of the animal. Attempts were then made to clothe some animals completely, but it was found exceedingly difficult to keep the clothing on, particularly the trousers. One animal was, however, kept protected as to her legs, and not a single warble was found on her. It occurred to the professor that there was nothing to prevent the trousered cattle from licking the legs of the others, so in a further experiment the clothed animals were kept in a separate field. Another method tried was to keep some animals muzzled so that they could not lick either their own legs or those of others. The muzzled animals, however, had warbles. The whole series was therefore rather inconclusive. One serious difficulty in attempting to use the experience of European experimenters is the fact that the American and European warble flies are not identical, although extremely similar.

PATENTS.

Apparatus for Stretching Hides, Skins and the like. U. S. Patent 1,105,824. ROBERT NOBLETT, England.

Leather Dryer. U. S. Patents 1,106,271 and 1,106,272. ELWOOD B. AYRES, Philadelphia, Pa.

Setting-out Machine. British Patent 9,192. B. & J. WRIGHT, Leeds, England.

Tanning Process. British Patent 7,138. J. Y. JOHNSON, London, for Badische Anilin und Soda Fabrik. Skins are tanned by means of aqueous solutions of amorphous aromatic sulphonic acids which are free from phenolic hydroxyl groups and can precipitate glue or gelatine from a solution. The acids employed may be of high molecular product and contain several benzene or naphthalene residues. Suitable compounds are those obtained by reacting with formaldehyde on a naphthalene sulphonic acid in the presence or absence of condensation agents; or the bodies obtained by sulphonating the resins derived from formaldehyde and naphthalene may be employed. Examples are given of the methods of preparing tanning compounds by sulphonation of naphthalene, carbazole, and retene with sulphuric acid and condensing the products with formaldehyde. B-naphthalene-sulphonic acid is also condensed with sulphur chloride.

Process of Tanning Leather. U. S. Patent 1,107,759. JAMES C. CLEARY, Chicago, Ill. The product of destructive distillation of "Oachita" cretaceous lignite is the basis of the tanning liquor. Tanning extract is added at the beginning and at intervals of a week. The whole time required is about 4 weeks.

Machine for Working Hides & Leather. U. S. Patent 1,107,640. HENRY ALEES, Milwaukee, Wis.

Digitized by Google

Instrument for Removing Hides. U. S. Patent 1,110,859. H. M. ASHTON, Australia.

Compounds for Tanning Skins and Process of Making Them. U. S. Patent 1,107,107. LEOPOLD POLLAK, Aussig, Austria-Hungary, assignor to Badische Anilin und Soda Fabrik. The new compounds are derived from a monohydroxy phenol, sulphuric acid and a carbohydrate. They are amorphous, contain sulphur, are soluble in water, yield solutions giving deep coloration with ferric alum, precipitate glue solutions and tan skins without destroying them even in solutions of normal acidity at 20° Bé. On being shaken with ammonium acetate and a little alum, these solutions give a flocculent precipitate. One set of proportions is 5 parts phenol, 5 parts 98 per cent. sulphuric acid and 1 part grape sugar.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. IX NOVEMBER, 1914 No. 11

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1914, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VEITCH, } . . . Past Presidents

OFFICERS, 1913-'14

PRESIDENT—W. K. ALSOP, Ridgway, Pa.
VICE-PRESIDENT—C. W. NORRIS, 80 South Street, New York, N. Y.
SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.
COUNCIL—A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y
LLOYD BALDERSTON, Ridgway, Pa.
C. R. OBERFELL, Harrisonburg, Va.
T. A. FAUST, 323 Academy Street, Newark, N. J.

CHANGES OF ADDRESS.

J. W. Leonard, to 154 N. Perry St., Titusville, Pa.
H. C. Merrill, to 468 Central St., Lowell, Mass.
George W. Priest, to 78 Beach St., East Orange, N. J.

ELEVENTH ANNUAL MEETING.

The Eleventh Annual Meeting of the American Leather Chemists Association, in conjunction with the Annual Meeting of The National Association of Tanners, takes place at the Hotel Sherman, Chicago, Ill., on Wednesday, Thursday, Friday and Saturday, October 28, 29, 30 and 31, 1914.

Digitized by Google

The program as sent out by the Secretary is as follows:

WEDNESDAY MORNING, OCTOBER 28, 1914.

Opening remarks by the President.....W. K. ALSOP
Report of the Secretary-Treasurer.....H. C. REED
Committee Reports.

WEDNESDAY AFTERNOON, OCTOBER 28, 1914.

Address .....GEORGE A. KERR
"Color Valuation of Tanning Materials."
Address ..... LLOYD BALDERSTON
"Laboratory Apparatus for Leaching Experiments."
(Prepared by Lloyd Balderston and W. K. Alsop.)
Address .....F. A. LOVELAND
"The Relation Between Green Salted Weight and White Weight of Various Portions of the Hide."
Address .....E. H. BACHTENKIRCHER
"Lime."

THURSDAY MORNING, OCTOBER 29, 1914.

Committee Reports.
Address .....DR. ALLEN ROGERS
"Dyes and Dyestuffs."
Address .....JOHN H. YOCUM
"Leach House Efficiency."

THURSDAY NOON, OCTOBER 29, 1914.

Luncheon.
Round Table Discussions.

THURSDAY AFTERNOON, OCTOBER 29, 1914.

Address .....C. C. SMOOT, III.
"Sewage Disposal and Use of Tannery Wastes."
Address .....A. ROTH
"A Resumé of the Methods of Tannery Sewage Disposal."
Address .....DR. ALLEN ROGERS
"The Bating of Hides and Skins."
Executive Committee of The National Association of Tanners at 6.30.
Group Meetings.

FRIDAY MORNING, OCTOBER 30, 1914.

Committee Reports.
Address .....THOMAS A. FAUST
"The Availability of Tannins in Liquors of Various Strengths."

Digitized by Google

Address .....W. K. ALSOP
"Determination of Insolubles in the Analysis of Tannin Extracts."
Address .....SIGMUND SAXE
"Spruce Extract."
Address .....F. P. VEITCH
"The Clarification of Leather Extracts for the Determination of Reducing Sugars."
(Prepared by F. P. Veitch and J. S. Rogers.)
General Meeting of The National Association of Tanners.

FRIDAY NOON, OCTOBER 30, 1914.

Lunch Allied Trades.

FRIDAY AFTERNOON, OCTOBER 30, 1914.

Joint Meeting of the American Leather Chemists Association and The National Association of Tanners. Discussion, Tanning School, etc.

SATURDAY MORNING, OCTOBER 31, 1914.

Executive Session of the American Leather Chemists Association.
Election of Officers.

THE COLOR VALUATION OF TANNING MATERIALS.*

By George A. Kerr.

To those who have endeavored from time to time to bring a method for the visual color comparison of vegetable tanning materials to a successful issue, the papers by H. R. Procter[1] (*Shoe and Leather Reporter,* March 19th, 1914) and H. C. Reed (JOURNAL A. L. C. A., May, 1914) are of much interest and contain suggestions which worked out to finality should materially assist in either establishing a standard procedure for skin or hide color tests or furnish sufficient reason for abandoning this phase of the subject.

Following up the observations of Procter and Reed our experience indicates that if a comparative color test is really required, it is not so difficult to obtain as would appear from the volume of discussion there has been on the question. Here let me say I do not forget I have expressed a belief that skin or color tests would never be satisfactory. In explanation, however, I particularly referred to their arbitrating value to the

* Read at the A. L. C. A. convention, Chicago, October 28, 1914.

Digitized by Google

tanner or extract manufacturer, even were they comparative, and not to the possibility of demonstrating mere color or tone differences. Looking at the causes of failure to secure comparative results, one of the most important has been the application of the test from a tanning standpoint instead of recognizing that it is primarily a dye-test. If considered as such there appears to be no insurmountable obstacle to obtaining the desired results, and if the procedure to be outlined later is carried out with ordinary care and within reasonable limits, fair concordance may be maintained. Considering these tests as dye-tests and not tanning ones, the first principle to be observed is the quantitative relation of the matter combining with hide to the weight of dry hide substance employed for the test.

Up to this time the various attempts to bring about concordance have employed either at one application or progressively an excess of these combining substances or tannin, with the result that even in the absence of other disturbing factors, the phenomenon of selective absorption was given full play, and the tests considered complete when tanned through, irrespective of whether the hide had precipitated the combining constituents in the proportions in which they existed in the extract or liquor.

It having been demonstrated that the coloring principles of various materials do not combine as rapidly as the true tannin, it must be obvious that hide in the presence of an excess of tannins and coloring matter will be tanned long before it is dyed, in the true proportion of the components. It has been claimed that the strength of solutions may be widely varied without materially affecting the color of the test. If this is true it only proves my claim that selective absorption does occur, for if tannin and coloring were precipitated in their proper proportions, the color of the test would vary with the strength of the solution the same as any other dye-test. This, however, is a point that does not justify much argument, as I hope to make clear.

To obtain a true representation of the color which a given tanning material will yield on hide, it is absolutely essential that the hide-substance and combining matter (or according to analyses tannin) be so proportioned that the hide will com-

Digitized by Google

pletely precipitate or combine with all the solution contains, or, more briefly, detannize it.

Next to the observance of this principle, a further necessity is a base material of fairly uniform character and of a nature resembling as closely as possible the practical condition of hide before it is tanned. Any skin or hide treated by chemicals which even to a slight degree have entered into permanent combination with or altered the hide-substance is unsuitable, as it rarely can be brought back to a condition which even approximates that of a hide emerging from the beam house.

These limits of suitability are so narrow and well-defined that the use of pickled sheep-skins or partially tawed or chromed hide or skin is at once eliminated, and it is difficult to understand the persistence of the endeavors to make such material answer the purpose, especially when more suitable materials are available.

The best base for these tests is the grain split from limed green salted hides or calf skins, which if split to a 2½ or 3 ounce substance, and prepared with the same care and attention to cleansing that hides are for the manufacture of hide-powder, will fulfill every demand.

Such hide should not be difficult to procure, and with the demand that a color test accompany every analysis, the requirements are great enough to warrant their preparation and distribution from a central source on the same basis as we now are supplied with hide-powder. The selection of hides and their preparation being in the hands of one concern should insure a practical limit of uniformity. The portion of the hide grain to be used should also be limited to that corresponding to the trim for bends.

It may be suggested that high cost would be an objection, but when the loss from discarding impossible skins and such portions as cannot be used is considered, to say nothing of sending out results which do not mean anything, the cost is unimportant.

Assuming for the moment this system can be established, this hide may be furnished in either of two ways; in the wet state preserved in the boro-phenol solution employed by Small in this country, or according to the provisional method of the I. A. L. T. C. abroad. It could also be furnished in the dry

Digitized by Google

state after dehydration according to the method outlined by Armstrong.

After using the grains furnished by Small for some years, we find them not only the most satisfactory but the only material available here which fulfills our requirements. The dehydrated skin we cannot recommend, as it is unfortunately permanently changed by the tawing effect of the alcohol and ether,—so much so that though it wets down readily, prolonged soaking in water does not restore it to anything like its original condition. The gelatin becomes fixed to an extent which lessens its capacity for combining with the tanning and coloring matters, while it seems to exert a greater selective quality in their precipitation than the hide preserved in boro-phenol solution. Numerous tests demonstrate that the color principle is scarcely taken up at all.

The method now employed in our laboratory is as follows:

1st. A sufficient number of moisture determinations of the hide in use are made to establish within approximate limits the actual dry hide contents. The portions taken for drying being washed on the shaker three times in distilled water for as many 15 minute periods.

The figure thus obtained is used to control the tannin strength of the solution employed for the test. It is sufficiently accurate to control tests as long as the current skin lasts. The figure should, however, be re-established with every new grain.

2nd. (a) Cut a piece of grain the size desired, and after washing as above, shake off free water, weigh, and calculate its dry weight.

(b) Make up a solution of which 200 cc. will contain 80 per cent. as much tannin as the dry weight of the grain to be colored.

(c) Two hundred cc. of the solution is then measured into a shaker bottle, the grain entered and shaking proceeded with until the solution is practically detannized, which will be in 6 or 7 hours, or in the case of bark extracts somewhat longer. The dry hide employed should not be less than 2 or more than 2.5 grams. To be under this limit attenuates the solution to the extent of prolonging the coloring unduly. While it is not so important, it is better not to exceed 2.5 grams, which with grains split the proper thickness gives about 20 sq. in. of skiver.

Digitized by Google

The coloring or tanning completed, the grain, after squeezing by hand, may be washed in distilled water on the shaker, or it may be placed flat in a shallow dish, covered with water and left for 6 or 8 hours.

The immersion in water merely removes the non-tannin solution held by the grain, but does not wash out the fixed color or tannin.

The uniform drying of the grains has been found difficult and unsatisfactory when proceeded with in the ordinary way. We, therefore, have abandoned it for dehydration with alcohol, and removing the latter with ether.

This is carried out in the following manner:

Take the colored grains from the distilled water, squeeze by hand, and smooth by gently stretching in every direction, lay on a dry, clean, folded towel, roll up, and after allowing the towel to absorb the water for 15 min., place in 150 cc. of 95 per cent. alcohol in a shaker bottle and shake for 10 min., then remove but do not squeeze, spread evenly again on a folded towel, roll up for a few minutes and then immerse for 30 min., with occasional shaking, in ether contained in a wide-mouth flask or bottle. Upon removal from the ether, gently stretch until dry, which takes only a few minutes.

Assuming, for the sake of argument, that it is possible to obtain comparative color tests on hide, the question of their value to the tanner and extract maker must be considered. Although this is a more important point to settle for good than the method of making tests, past discussion does not seem to have led to any conclusion. Opinions on the subject differ widely as to the value of these tests, though I think the majority of those who have given the subject much thought will agree an interpretation of the difference in color between two or more skivers is hard to come at, and probably no two men would render the same interpretation. So far as proving useful in the direction of serving as an index on the final color of any given tannage, there can be no two opinions, as they will not do so, the color of the finished stock depending upon yard conditions to an extent sufficient to eliminate the skiver as a guide in selecting tanning materials to produce a preconceived result.

Digitized by Google

Comparative skivers will, however, indicate a difference in color between various makes or grades of tanning material of the same kind. They will also, after a fashion and under certain conditions, check up deliveries on contracts extending over long periods, but this is about the limit of their usefulness.

When it comes to adjusting values between buyer and seller they afford no basis of calculation, and to neither tanner nor extract maker do they make clear in what element of color a tanning material is deficient, thereby failing to assist in accomplishing the desired demonstration of the color elements to be retained or discarded.

It has been claimed that these tests are useful in individual laboratories, which is a matter to be decided by the individual chemist. Nevertheless, I have yet to see an acceptable rendering of the conclusions arrived at, and it would be interesting to know how the chemist who finds these skivers useful makes a report of the color quality of a tanning material based upon findings thus obtained.

Usually the skiver test is made at the same time as the analysis, and when both are completed the skiver is pinned to the copy of the analytical results and handed over without comment, the analyst wisely leaving the recipient to draw his own conclusions. Occasionally, when the skiver is exceptionally bad, an apology for a faulty skin will accompany the analysis, and in any event a poorly colored skiver is more often held, by the extract maker at least, to be due to an inferior skin than the tanning material, and in the absence of proof to the contrary, how can the tanner gainsay it?

To be of real value a color test must do more than render a mere visual demonstration of difference in color or shade, that is, the results to be of service to the tanner and tanning material producer must yield in mathematical terms the proportions of the elementary colors existing in the material examined, so that the color quality can be compared in the same way that tannin analyses are.

Objections have been taken to a mathematical expression of color value, but they were made at a time when the Lovibond tintometer was the only basis of such expression, and it must be

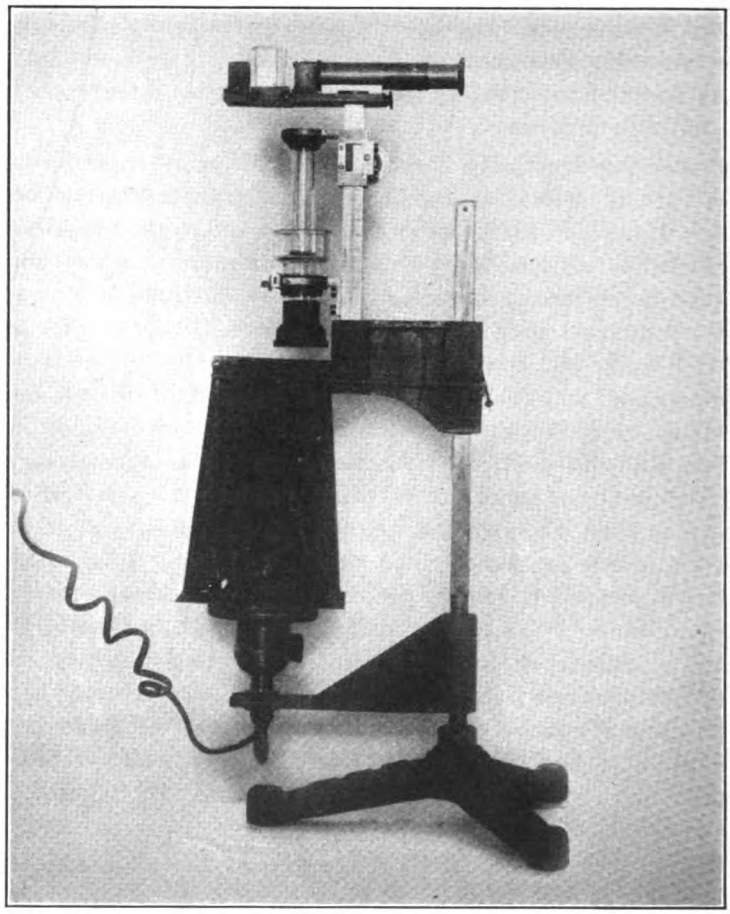
Digitized by Google

granted that anything like an accurate determination by this means is impossible. If, however, means were available whereby accurate color measurements could be made, there could be no more objection to reporting results in figures than there would be to any other analyses.

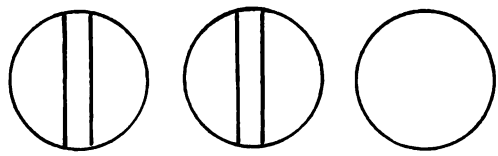
Proceeding upon this basis, I have for years experimented with various methods of making color determinations, and now believe I may announce that an instrument and method have been developed in my laboratory which promise more than any other method heretofore encountered. With this instrument we have for months past been able accurately to check up our factory control work, and have further proven its value by continued comparisons with skiver tests made as heretofore outlined. Without exception the new colorimeter has corroborated the skiver, with this difference: the instrument yields an analysis of the component primary colors which produce the color of the tannin solution, and shows in an intelligible manner why one extract is lighter or darker than another. Besides this, it furnishes a permanent record, against which comparisons may be made indefinitely. In extract making practice we find it of great value, it enabling us to locate with little trouble the source of color disturbance by showing which elements are deficient or in excess, and for tannery control it should prove even more valuable, as it will not only check up color changes in the yard, but indicate to a considerable extent the progress of sappage in straight or blended liquors.

Procter, having demonstrated the failure of the tintometer, suggested the use of a colorimeter made by Schmidt and Haensch of Berlin, which seemed more or less promising until it was shown it had the same defect as the tintometer in having to rely upon an arbitrarily numbered series of colored glasses which, like the tintometer, failed to interpret the elementary color combination, and, besides, it was found duplicate sets could not be obtained, which of course was fatal to the method. Our experiments with the S. & H. colorimeter, however, led us to believe that properly modified the apparatus might be made feasible, and almost simultaneously with Procter's suggestion we had begun experiments with color solutions in place of glasses for

Digitized by Google



Schmidt & Haensch colorimeter. Modified by Geo. A. Kerr.

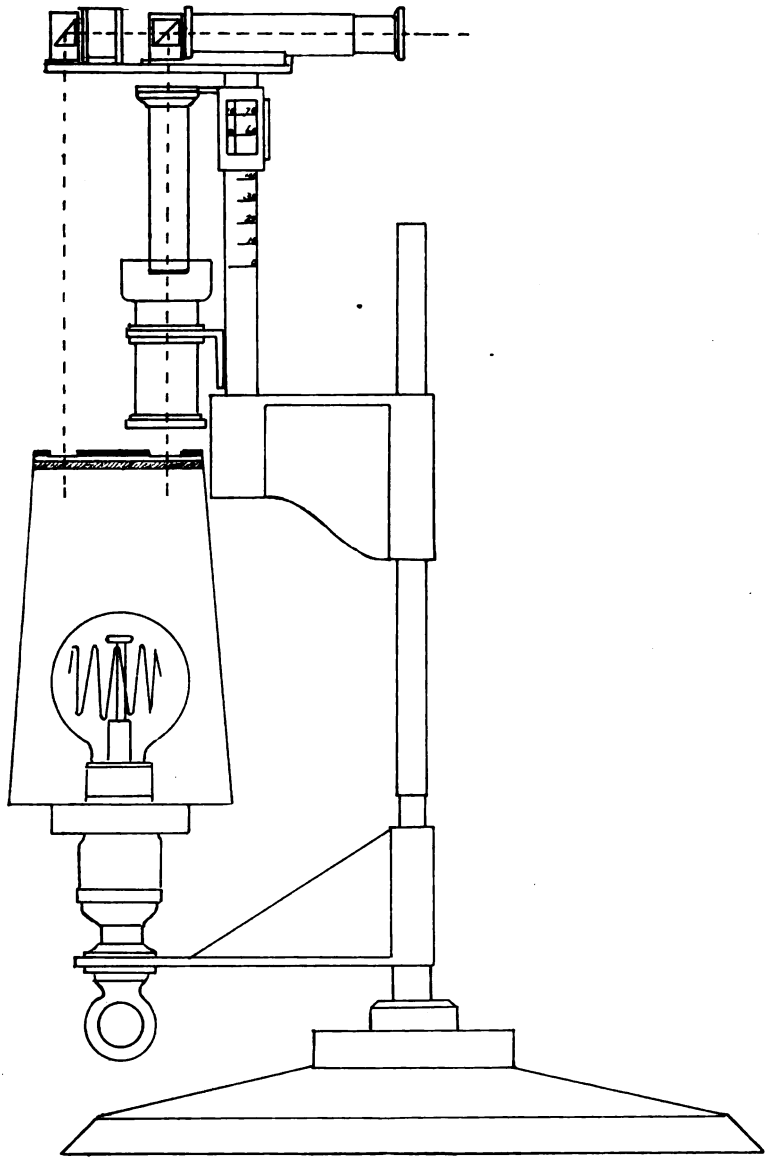


1 View through 1 cm. cell

2 View through color sol.

3 View when colors match

Digitized by Google



Schmidt & Haensch colorimeter. Modified by Geo. A. Kerr.

Digitized by Google

matching the tannin solutions to be tested. Before reaching the actual color matching stage, however, several minor obstacles such as uniform illumination, etc., had to be overcome, so that by the time we arrived at the present stage of development we had practically reconstructed the instrument. I will not attempt to give a technical description of the instrument, as in the absence of a demonstration it would be hard to follow. I will, however, attempt to explain why I believe it to be a step forward in the solution of color determination.

In order to make this explanation clear, it is necessary to show wherein the tintometer and Procter's modified use of the S. & H. colorimeter fail to accomplish the purpose sought after.

The tintometer primarily depends upon accurately combining several colored glasses representing the primary colors to match the color of a tannin solution of known strength one centimeter thick. These glasses are numbered arbitrarily, and do not seem to bear any direct relation to one another as to intensity of color. That is to say two No. 3 glasses do not equal in intensity one No. 6, and so on, therefore it is impossible to compare or obtain any intelligent idea of the color intensity of a solution from the index numbers of the glasses employed in matching it. This fault is alone sufficient to condemn the tintometer, but worse than this is the fact that it is next to, if not quite, impossible to obtain a true color match by any possible combination of glasses for at least two reasons; first, the ultimate match point usually falls between the limits of the fractional glasses, and second, as these glasses are colored on the surface only, there is a considerable error introduced by the color of the inside layer of clear glass, which varies with the number of glasses employed in each specific determination, and for which correction cannot be made without resorting to an equally arbitrary series of colored correction glasses.

Procter has called attention to this discrepancy by explaining it in a somewhat different manner, thus I think he states that assuming a match is found, and the strength of the solution and number of glasses are then doubled, the apparent color match disappears, which is true, the reason being, however, that the color intensity of the glasses does not increase in constant multi-

Digitized by Google

ples of their lowest fractional numbers, so that a reading giving a solution of, say 9 Y, 3 R, 1 B is as liable as not to become 25 Y, 9 R and 3 B when the strength is doubled.

The selection of the S. & H. colorimeter by Procter was perhaps the most important feature of his attempt to better the tintometer, but the retention of the glasses as a standard of measurement blocked any material improvement, unless it was that by securing a variable depth of solution column, much finer distinctions of color could be detected. In addition to this, Procter's proposed method gave somewhat confusing results, owing to the double set of figures, which consisting on the one hand of a color reading and on the other of the tannin content per liter to produce the color made comparisons difficult if not impossible, thus my laboratory was never able to tell whether an extract of, say, 8 Y, 1.5 R and 0.5 B at 3.5 grams tannin per liter was of better color than one reading 7 Y, 2 R and 1 B with 4.5 grams tannin per liter.

Besides the defects cited, I found the question of illumination a source of great trouble, being inadequately provided for in either of the instruments referred to, but after somewhat prolonged experimentation, we succeeded in developing a device which gives a fairly white light of sufficient uniformity to be workable. With this accomplished, I proceeded to reverse the Procter method by placing a cubic cetimeter cell of the solution to be tested in front of the outboard prism where the colored glasses had been previously used, and employed the cylinder for containing the mixture of primary color solutions, *i. e.*, yellow, red and blue. The solutions are made up of known strength from specially prepared aniline colors and run into the cylinder from burettes, note being taken of the quantity of each employed, and endeavor being made to match as nearly as possible the color of the solution in the centimeter cell. A preliminary test is first made to determine if there is a column depth at which the colors match. Failing this, a further quantity of the color needed is added until a match is found. The volume of color solutions and the depth of column at which the match was found is recorded; finally the total column length of the color solution in the cylinder is measured. With these data it is then possible to

Digitized by Google

calculate the number of cubic centimeters of each color necessary to match the solution tested, or, if desired, the weight of the coloring matter equivalent to that in one cubic centimeter of the solution.

The following formulae illustrates the simplicity of calculating results:

Match column length × cc. of color solution ÷ total column length = cc. of color solution equivalent to 1 cc. of tannin solution,

thus

3.5 cm. match column length × 8 cc. color solution ÷ 6 cm. total column length = 4.66 cc.,

yellow, red or blue as the case may be.

To correct the color to a standard tannin content, multiply color found by desired standard strength and divide by actual tannin strength, thus:

Color 4.66 × standard strength 0.5 per 100 cc. ÷ actual strength 0.4 per 100 cc. = 5.82 cc. of the color in 1 cm. cell.

The final test of the value of this instrument and method lies in the possibility of obtaining actual color duplicates with color solutions representing as nearly as possible the primary colors of the spectrum.

That this is accomplished seems proven by the fact that I find the column depth of the artificial solution increases or decreases in direct ratio to the strength of the solution tested; thus a solution matching at 3 cm. column depth becomes 6 cm. when the strength of the solution in the centimeter cell is doubled, or 1.5 cm. when it is diluted one-half, the color match meantime being maintained.

So far we have not found either a tannin solution or an artificial one we could not match with great delicacy.

The method thus not only permits of the results of comparative color measurements being rendered in an intelligible form, but obviates the necessity of using tannin solutions of fixed strength; that is, the usual filtered analytical solution may be tested and the results corrected back to any tannin strength desired.

As the question of time is an important factor in many lab-

Digitized by Google

oratories, it is perhaps as well to say a determination can be made in 5 to 7 min., and while the adjusting of the color solution may seem to involve some trouble, my own experience and that of my assistants proves that it is not at all difficult to become adept at mixing the primary color solutions to the color desired.

The question of the stability and uniformity of the aniline color solutions gave us some concern, but I find that by using what are known as the "Pinotype" colors, manufactured of great purity and stability for color photography, any likely trouble on this score is eliminated. The makers guarantee the solutions to be stable and of unchanged color, even after months of exposure to light, and as a few grams of each will last any laboratory a year, the distribution of a few pounds would establish a standard for at least that time throuhgout the country. The general supply could be renewed from a fresh lot from time to time and a uniform standard thus maintained indefinitely.

In the absence of a description of the technical construction and operation of the instrument, the accompanying photo and drawing will doubtless assist to a full understanding of it.

THE RELATION BETWEEN GREEN SALTED WEIGHT AND WHITE WEIGHT OF VARIOUS PORTION OF THE HIDE.*

By F. A. Loveland.

The subject matter of this paper may be more a matter of curious interest than of real value, but never having noticed any data on the subject and having occasion to gather the statistics herewith given, I present them in the hope that they may be of use to some one.

The method pursued in gathering the data is as follows: The hides taken were green salted hides, mostly packers, and were cropped in the hair, in the condition in which they were received at the tannery. After cropping, the various parts were weighed and calculated to the invoice weight of hide paid for, each portion of hide standing its proportion of loss from the invoice weight.

* Read at A. L. C. A. convention, Chicago, October 28, 1914.

Digitized by Google

The various portions of hide were then processed through the beam-house together, each portion receiving the same treatment as to washing, soaking, liming and so forth, except that the beam-house together, each portion receiving the same treat- bellies and heads were hand fleshed. The bends were unhaired with the Leidgen machine, and the shoulders, bellies and heads by hand.

After unhairing, the different parts of the hide were washed and drained, then weighed to ascertain the white weight, then tabulated for comparison with the green salted weight, the results obtained are shown in the following table:

	No. pieces	Invoice weight of hide	Per cent. of total hide	White weight of hide	White weight per cent. of invoice weight
Whole hide	3,638	108,237	100.00	125,391	115.8
Bends	7,276	52,625	48.62	60,096	114.4
Shoulders	7,276	18,806	17.37	24,920	132.5
Bellies	7,276	26,441	24.48	29,937	113.2
Heads	7,276	10,365	9.57	10,438	100.7

In explanation of these figures it may be stated that in cropping the hides it was intended that the bend should equal 50 per cent. of the weight of the whole hide. The tabulated result shows 48.62 per cent. a difference of 1.38 per cent. The belly was to equal 25 per cent., and gave 24.48 per cent., a difference of 0.52 per cent. The shoulder should equal 15.00 per cent., and gave 17.37 per cent., a difference of 2.37 per cent. The head should equal 10.00 per cent., and gave 9.57 per cent., a difference of 0.43 per cent. Thus showing that hides can be cropped in the hair very closely to a fixed standard. The whole hide yielded in white weight 115.8 per cent., while the bends gave 114.4 per cent., a difference of only 0.6 per cent. The bellies gave 113.2 per cent., a difference of 2.6 per cent. The shoulders gave 132.5 per cent., a difference of 16.7 per cent. The heads gave 100.7 per cent., a difference of 15.1 per cent.

It will be noted that the great departure from the white weight of the whole hide is with the shoulder and head portions, a result which confirms previous experience with shoulders and explains the reason for this test; for having occasion to cut the shoulders from a number of lots of hides in the white and sell them to a separate tanning operation, the resultant yield of

Digitized by Google

leather from the shoulders was so low as to lead to the undertaking of this test conducted on a scale large enough to be of moment in proving the relation between green salted weight and white weight of the various portions of the hide.

DETERMINATION OF INSOLUBLES IN THE ANALYSIS OF TANNIN EXTRACTS.*

By W. K. Alsop.

The council has asked for some data in reference to tests of tanning materials when a stronger solution than that called for by the Official Method is used. For several years we have made the determination of total solids and soluble solids with solutions of extracts made up ten times as strong as the solution usually used. That is, if 15 grams per liter of extract is used for the ordinary analysis, we also make the determinations mentioned with a solution made on the basis of 150 grams per liter.

The usual procedure is to take the amount necessary to make 500 cc. of solution, dissolve as in the official method, rapid cooling in many cases being the most satisfactory. After being made to the mark, 100 cc. is quickly removed with a pipette having about a ⅛ in. opening. This amount is diluted to 1 liter and 100 cc. used for total solids. The remainder of the strong solution is then used for the determination of soluble solids, the filtration being carried out as per the official method. Either 100 cc. or 50 cc. is diluted to 1,000 cc. or 500 cc. as the case may be, and 100 cc. of the diluted liquor used for evaporation. The total solids found in this way usually agree within a few tenths per cent. with that found by the official method, and we usually report simply the percentage of insolubles shown under these conditions as well as by the Official Method. We occasionally have extracts which filter very slowly by this method. There are also some extracts with which the stronger solution filters more rapidly than those of official strength. The barkometer degree of the stronger liquors usually is from 18 to 30, depending upon the tannin content of the extract.

While it is true that the insolubles shown in many cases are somewhat in proportion to those obtained by the usual analysis,

* Read at the A. L. C. A. convention, Chicago, October, 1914.

Digitized by Google

there is often information of considerable value indicated. This is especially true with some materials, among them being treated extracts which give a practically clear solution when diluted as in the official method, but may show considerable precipitation in a stronger liquor.

Following are some of the results obtained by this method; also the insolubles found by the usual analysis.

Kind	Per cent. total solids	Per cent. insolubles analysis sol.	Per cent. insolubles sol. 10 times stronger
Quebracho	76.68	7.32	24.03
Quebracho	79.79	6.80	24.00
Quebracho	78.56	5.93	22.93
Quebracho	77.50	6.63	19.25
Quebracho	76.50	5.09	17.38
Quebracho	77.90	7.25	17.14
Quebracho	77.33	5.71	17.09
Quebracho	76.62	6.03	15.87
Quebracho	78.00	4.72	15.20
Quebracho	75.90	5.33	12.62
Quebracho	78.00	4.19	11.19
Quebracho	48.45	4.26	15.24
Quebracho	48.28	1.40	7.63
Quebracho	47.61	0.21	3.33
Quebracho	48.66	0.55	2.27
Quebracho	47.84	0.50	0.71
Myrobalan	85.75	2.66	7.35
Myrobalan	52.72	2.00	1.94
Cutch	83.05	4.98	14.68
Cutch	79.09	4.29	7.84
Cutch	81.97	1.34	5.52
Cutch	75.10	1.15	5.31
Chestnut	47.51	1.87	5.00
Chestnut	42.00	0.68	3.82
Chestnut	40.31	0.97	2.48
Chestnut	45.79	1.04	2.83
Chestnut	45.57	1.63	3.30
Chestnut	48.59	1.53	2.42
Chestnut	45.83	0.46	2.30
Chestnut	44.03	0.01	1.63
Chestnut	93.50	1.57	3.93
Chestnut	93.78	0.23	3.90
Chestnut	94.35	0.60	3.00

Elk Tanning Company Laboratory,
Ridgway, Pa.

Digitized by Google

REPORT OF 1914 COMMITTEE ON "EXTRACTION: SUGGESTED USE OF ALUNDUM THIMBLE."

By J. M. Seltzer, Chairman.

The work assigned to this committee was that of extraction along the lines suggested by Mr. F. H. Small, (JOUR. A. L. C. A. Jan., 1914), using alundum thimbles for holding the charge of tanning material. The thimbles used by this committee were kindly furnished by the Norton Company and fulfill the requisites for their successful operation, as described by Mr. Small. The size of these thimbles is 1⅞ in. diameter by 6 in. long and are listed by Norton Company as No. 9418.

In order to carry on the work it was decided to send out two bark samples each of which should be extracted, in one case without and the other with the use of the alundum thimble.

The following samples were sent out to those members who consented to serve on the committee.

No. 1—Hemlock bark.
No. 2—Oak bark.

Reports have been received from the following:

L. A. Cuthbert, Elk Tanning Co., Ridgway, Pa.
C. R. Oberfell, L. M. Richeson, England, Walton Lab., Harrisonburg, Va.
F. H. Small, Graton, Knight Mfg. Co., Worcester, Mass.
J. M Seltzer, Kistler, Lesh & Co., Lock Haven, Pa.

The directions sent out to the collaborators were as follows:

INSTRUCTIONS.

The following extractions and analyses are to be made according to the Official Method. A. L. C. A., 1914.

1. Make duplicate extractions of hemlock bark without using alundum thimble, analyze each solution. Use 38 grams hemlock bark per liter.
2. Make duplicate extractions of hemlock bark using the alundum thimble, analyze each solution. Use 38 grams hemlock bark per liter.

Digitized by Google

3. Make duplicate extractions of oak bark without using alundum thimble, analyze each solution. Use 34 grams oak bark per liter.

4. Make duplicate extractions of oak bark using alundum thimble, analyze each solution. Use 34 grams oak bark per liter.

5. If enough of the bark samples remain after doing the above work the chairman would be pleased to have results on extraction as suggested by R. H. Wisdom, JOURNAL A. L. C. A., March, 1913, following Official Method with exception of 6 hours continuous extraction instead of 14 hours.

The Teas extractors were used by all collaborators. The results given by those co-operating are shown in the following tables.

Digitized by Google

TABLE I.—AIR DRY BASIS. SAMPLE NO. 1. HEMLOCK BARK. WITHOUT THIMBLE.

	Analyst	Analysis No.	Total solids Per cent.	Soluble solids			Insolubles Per cent.	Non-tannins				Tannin Per cent.	Moisture Per cent.	Purity Per cent.	Tannin per 100 cc. sol. Grams
				Per cent.	Time to collect filtrate Min.	Appearance of filtrate		Per cent.	Moisture in hide powder Per cent.	Equivalent dry hide used Grams	Appearance of filtrate				
1	L. A. Cuthbert.....	1	—	—	—	—	—	—	—	—	—	—	—	—	—
		2	21.57	16.69	590	Clear	4.88	6.76	72.85	12.76	Tur'd	9.93	9.75	59.50	0.3873
		Av.	21.57	16.69			4.88	6.76				9.93	9.75		
2	G. R. Oberfell.....	1	20.51	17.16	540	Clear	3.35	6.69	72.35	12.86	Sl. op.	10.47	9.69	61.01	0.3979
	L. M. Richeson	2	20.54	17.12	540	Clear	3.42	6.48	72.35	12.86	Sl. op.	10.64	9.69	62.15	0.4043
		Av.	20.53	17.14			3.39	6.59				10.55	9.69	61.55	0.4009
3	F. H. Small	1	22.21	17.60	440	Clear	4.61	6.80	72.96	12.71	Yel.	10.80	10.13	61.36	0.4104
	V. J. Mlejnek	2	20.93	16.80	460	Clear	4.14	6.42	72.70	12.83	Yel.	10.38	10.04	61.93	0.3944
		Av.	21.57	17.20			4.38	6.61				10.59	10.09	61.57	0.4024
4	J. M. Seltzer	1	22.17	18.12	345	Clear	4.05	6.89	73.00	12.56	Clear	11.23	10.05	61.99	0.4267
		2	21.46	17.70	345	Clear	3.76	6.68	73.00	12.56	Clear	11.02	10.05	62.28	0.4188
		Av.	21.82	17.91			3.91	6.79				11.12	10.05	62.09	0.4228
	General average		21.37	17.24			4.13	6.69				10.55	9.90	61.19	
	Highest average		21.82	17.91			4.88	6.79				11.12	10.09	62.09	
	Lowest average		20.53	16.69			3.39	6.59				9.93	9.69	59.50	
	Greatest difference.....		1.29	1.22			1.49	0.20				1.19	0.40	2.59	

Digitized by Google

TABLE 2.—AIR DRY BASIS. SAMPLE NO. 1. HEMLOCK BARK. WITH THIMBLE.

	Analyst	Analysis No.	Total solids Per cent.	Soluble solids			Insolubles Per cent.	Non-tannins				Tannin Per cent.	Moisture Per cent.	Purity Per cent.	Tannin per 100 cc. sol. Grams
				Per cent.	Time to collect filtrate Min.	Appearance of filtrate		Per cent.	Moisture in hide powder Per cent.	Equivalent air-dry hide powder Grams	Appearance of filtrate				
1	L. A. Cuthbert	1	21.48	16.66	470	Clear	4.82	6.63	72.85	12.76	Tur'd	10.03	9.75	60.20	0.3811
		2	20.88	16.46	585	Clear	4.42	6.42	72.85	12.76	Tur'd	10.04	9.75	61.00	0.3820
		Av.	21.18	16.56			4.62	6.53				10.03	9.75	60.57	
2	C. R. Oberfell	1	19.15	16.00	540	Sl. op.	3.15	5.99	72.35	12.86	V. op.	10.01	9.69	62.57	0.3804
	L. M. Richeson	2	19.70	15.96	540	Sl. op.	3.74	5.95	72.35	12.86	Opal	10.01	9.69	62.72	0.3804
		Av.	19.43	15.98			3.45	5.97				10.01	9.69	62.64	0.3804
3	F. H. Small	1	21.02	16.73	380	Clear	4.29	6.06	72.72	12.82	Yel.	10.67	10.13	63.78	0.4055
	V. J. Mlejnek	2	20.56	16.65	397	Tur'd	3.91	6.19	72.96	12.71	Yel.	10.46	10.04	62.82	0.3975
		Av.	20.79	16.69			4.10	6.13				10.57	10.09	63.33	0.4017
4	J. M. Seltzer	1	20.62	16.80	510	Clear	3.82	6.39	73.00	12.56	Clear	10.41	10.05	61.97	0.3956
		2	21.10	17.37	510	Clear	3.73	6.64	73.00	12.56	Clear	10.73	10.05	61.80	0.4077
		Av.	20.86	17.09			3.77	6.52				10.57	10.05	61.85	0.4015
	General average		20.57	16.58			3.99	6.29				10.29	9.90	62.09	
	Highest average		21.18	17.09			4.62	6.53				10.57	10.09	63.33	
	Lowest average		19.43	15.98			3.45	5.97				10.01	9.69	60.57	
	Greatest difference		1.75	1.11			1.17	0.56				0.56	0.40	2.76	

Digitized by Google

TABLE 3.—ABSOLUTELY DRY BASIS. CALCULATED FROM TABLE 1. SAMPLE NO. 1 HEMLOCK BARK. WITHOUT THIMBLE.

	Analyst	Analysis No.	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Non-tannins Per cent.	Tannin Per cent.
1	L. A. Cuthbert	1	—	—	—	—	—
		2	23.89	18.49	5.40	7.49	11.00
		Av.	23.89	18.49	5.40	7.49	11.00
2	C. R. Oberfell	1	22.71	19.00	3.71	7.41	11.59
	L. M. Richeson	2	22.74	18.95	3.79	7.18	11.77
		Av.	22.73	18.98	3.75	7.30	11.68
3	F. H. Small	1	24.75	19.62	5.13	7.58	12.04
	V. J. Mlejnek	2	23.30	18.69	4.61	7.15	11.54
		Av.	24.03	19.16	4.87	7.37	11.79
4	J. M. Seltzer	1	24.64	20.14	4.50	7.66	12.48
		2	23.86	19.67	4.19	7.43	12.24
		Av.	24.25	19.91	4.34	7.55	12.36
	General average		23.73	19.14	4.59	7.43	11.71
	Highest average		24.25	19.91	5.40	7.55	12.36
	Lowest average		22.73	18.49	3.75	7.30	11.00
	Greatest difference		1.52	1.42	1.65	0.25	1.36

TABLE. 4.—ABSOLUTELY DRY BASIS CALCULATED FROM TABLE 2. SAMPLE NO. 1 HEMLOCK BARK. WITH THIMBLE.

	Analyst	Analysis No.	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Non-tannins Per cent.	Tannin Per cent.
1	L. A. Cuthbert	1	23.80	18.46	5.34	7.35	11.11
		2	23.13	18.21	4.94	7.11	11.10
		Av.	23.47	18.33	5.14	7.23	11.10
2	C. R. Oberfell	1	21.22	17.72	3.50	6.63	11.09
	L. M. Richeson	2	21.82	17.68	4.14	6.59	11.09
		Av.	21.52	17.70	3.82	6.61	11.09
3	F. H. Small	1	23.42	18.64	4.78	6.75	11.89
	V. J. Mlejnek	2	22.88	18.52	4.36	6.89	11.63
		Av.	23.15	18.58	4.57	6.82	11.76
3	J. M. Seltzer	1	22.92	18.67	4.25	7.10	11.57
		2	23.45	19.31	4.14	7.39	11.92
		Av.	23.19	18.99	4.20	7.25	11.74
	General average		22.83	18.40	4.43	6.98	11.42
	Highest average		23.47	18.99	5.14	7.25	11.76
	Lowest average		21.52	17.70	3.82	6.61	11.09
	Greatest difference		1.95	1.29	1.32	0.64	0.67

Digitized by Google

TABLE 5.—AIR DRY BASIS. SAMPLE NO. 2. OAK BARK. WITHOUT THIMBLE.

	Analyst	Analysis No.	Total solids Per cent.	Soluble solids			Insolubles Per cent.	Non-tannins				Tannin Per cent.	Moisture Per cent.	Purity Per cent.	Tannin per 100 cc. sol. Grams
				Per cent.	Time to collect filtrate Min.	Appearance of filtrate		Per cent.	Per cent. Moisture in hide powder	Equivalent dry hide used Grams	Appearance of filtrate				
1	L. A. Cuthbert	1	23.23	20.76	265	Clear	2.47	8.79	72.50	12.93	Tur'd	11.97	3.00	57.66	0.4070
		2	23.31	20.65	235	Clear	2 66	8.82	72.50	12.93	Tur'd	11.83	3.00	57.29	0.4022
		Av.	23.27	20.71			2.56	8.81				11.90	3.00	57.46	0.4046
2	C. R. Oberfell	1	22.68	20.22	275	Clear	2.46	8.42	72.35	12.86	Clear	11.80	3.41	58.36	0.4012
	L. M. Richeson	2	23.21	20.71	280	Clear	2.50	8.64	72.35	12.86	Clear	12.07	3.41	58.28	0.4104
		Av.	22.95	20.47			2.48	8.53				11.94	3.41	58.33	0.4060
3	F. H. Small	1	23.97	20.56	202	Clear	3.41	8.87	72.92	12.72	Clear	11.69	3.32	56.86	0.3975
	V. J. Mlejnek	2	23.95	20.50	315	Clear	3 45	8.79	72.70	12.83	Clear	11.71	3.39	57.12	0.3981
		Av.	23.96	20.53			3.43	8.83				11.70	3.36	56.99	0.3978
4	J. M. Seltzer	1	23.96	20 25	135	Clear	3.71	8.57	73.00	12.56	Clear	11.68	3.41	57.69	0.3971
		2	23.87	20.22	85	Clear	3.65	8.57	73.00	12.56	Clear	11.65	3.41	57.62	0.3961
		Av.	23.92	20.24			3.68	8 57				11.67	3.41	57.66	0.3968
	General average		23.53	20.49			3.04	8.69				11.80	3.30	57.59	
	Highest average		23.96	20.71			3.68	8.83				11.94	3.41	58.33	
	Lowest average		22.95	20.24			2.48	8.53				11.67	3.00	56.99	
	Greatest difference		1.01	0.47			1.20	0.30				0.27	0.41	1.34	

Digitized by Google

TABLE 6.—AIR DRY BASIS. SAMPLE NO. 2. OAK BARK. WITH THIMBLE.

	Analyst	Analysis No.	Total solids Per cent.	Soluble solids			Insolubles Per cent.	Non tannins				Tannin Per cent.	Moisture Per cent.	Purity Per cent.	Tannin per 100 cc. sol. Grams
				Per cent.	Time to collect filtrate Min.	Appearance of filtrate		Per cent.	Moisture in hide powder Per cent.	Equivalent dry hide used Grams	Appearance of filtrate				
1	L. A. Cuthbert	1	21.84	19.49	205	Clear	2.35	8.16	72.50	12.93	Tur'd	11.33	3.00	58.13	0.3852
		2	21.49	19.56	157	Clear	1.93	8.27	72.50	12.93	Tur'd	11.29	3.00	57.70	0.3839
		Av.	21.67	19.53			2.14	8.22				11.31	3.00	57.91	0.3845
2	C. R. Oberfell	1	21.59	19.17	275	Clear	2.42	7.87	72.35	12.86	Clear	11.30	3.41	58.95	0.3842
	L. M. Richeson	2	20.48	18.55	125	Clear	1.93	7.56	72.35	12.86	Clear	10.99	3.41	59.25	0.3737
		Av.	21.04	18.86			2.18	7.72				11.14	3.41	59.07	0.3788
3	F. H. Small	1	23.76	20.24	195	Clear	3.52	8.83	72.92	12.72	Tur'd	11.41	3.32	56.37	0.3879
	V. J. Mlejnek	2	23.87	20.25	240	Clear	3.62	8.78	73.70	12.83	Tur'd	11.47	3.39	56.64	0.3900
		Av.	23.82	20.25			3.57	8.81				11.44	3.36	56.49	0.3890
4	J. M. Seltzer	1	23.38	20.39	120	Clear	2.99	8.52	73.00	12.56	Clear	11.87	3.41	58.21	0.4036
		2	—	—	—	—	—	—	—	—	—	—	—	—	—
		Av.	23.38	20.39	120		2.99	8.52				11.87	3.41	58.21	0.4036
	General average		22.48	19.76			2.72	8.32				11.44	3.30	57.90	
	Highest average		23.82	20.39			3.57	8.81				11.87	3.41	59.07	
	Lowest average		21.04	18.86			2.14	7.72				11.14	3.30	56.49	
	Greatest difference		2.78	1.53			1.43	1.09				0.73	0.41	2.58	

Digitized by Google

TABLE 7.—ABSOLUTELY DRY BASIS. CALCULATED FROM TABLE 5. SAMPLE NO. 2. OAK BARK WITHOUT THIMBLE.

	Analyst	Analysis No.	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Non-tannins Per cent.	Tannin Per cent.
1	L. A. Cuthbert	1	23.94	21.40	2.54	9.06	12.34
		2	24.03	21.29	2.74	9.10	12.19
		Av.	23.99	21.35	2.64	9.08	12.27
2	C. R. Oberfell	1	23.48	20.94	2.54	8.72	12.22
		2	24.03	21.44	2.59	8.95	12.49
		Av.	23.76	21.19	2.57	8.83	12.36
3	F. H. Small	1	24.81	21.26	3.55	9.17	12.09
	V. J. Mlejnek	2	24.79	21.23	3.56	9.10	12.13
		Av.	24.80	21.25	3.56	9.14	12.11
4	J. M. Seltzer	1	24.81	20.96	3.85	8.88	12.08
		2	24.71	20.94	3.77	8.87	12.07
		Av.	24.76	20.95	3.81	8.88	12.07
	General average		24.33	21.18	3.15	8.98	12.20
	Highest average		24.80	21.35	3.81	9.14	12.36
	Lowest average		23.76	20.95	2.57	8.83	12.07
	Greatest difference		1.04	0.40	1.24	0.31	0.29

TABLE 8.—ABSOLUTELY DRY BASIS. CALCULATED FROM TABLE 6. SAMPLE NO. 2. OAK BARK. WITH THIMBLE.

	Analyst	Analysis No.	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Non-tannins Per cent.	Tannin Per cent.
1	L. A. Cuthbert	1	22.52	20.09	2.43	8.42	11.67
		2	22.15	20.17	1.98	8.52	11.65
		Av.	22.34	20.13	2.21	8.47	11.66
2	C. R. Oberfell	1	22.35	19.85	2.50	8.15	11.70
	L. M. Richeson	2	21.20	19.20	2.00	7.83	11.37
		Av.	21.78	19.53	2.25	8.00	11.53
3	F. H. Small	1	24.57	20.94	3.63	9.14	11.80
	V. J. Mlejnek	2	24.71	20.97	3.74	9.09	11.88
		Av.	24.64	20.96	3.69	9.12	11.84
4	J. M. Seltzer	1	24.21	21.12	3.09	8.82	12.30
		2	—	—	—	—	—
		Av.	24.21	21.12	3.09	8.82	12.30
	General average		23.24	20.44	2.80	8.60	11.84
	Highest average		24.64	21.12	3.69	9.12	12.30
	Lowest average		21.78	19.53	2.21	8.00	11.53
	Greatest difference		2.86	1.59	1.48	1.12	0.77

Digitized by Google

TABLE 11.—AIR DRY BASIS. SUMMARY OF AVERAGE ANALYSES. SAMPLE NO. 1 HEMLOCK BARK.

	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Non-tannins Per cent.	Tannin Per cent.	Purity Per cent.
Without thimble	21.37	17.24	4.13	6.69	10.55	61.19
With thimble	20.57	16.58	3.99	6.29	10.29	62.07
Difference	0.80	0.66	0.14	0.40	0.26	0.88
ABSOLUTELY DRY BASIS.						
Without thimble	23.73	19.14	4.59	7.43	11.71	
With thimble	22.83	18.40	4.43	6.98	11.42	
Difference	0.90	0.74	0.16	0.45	0.29	

TABLE 12.—AIR DRY BASIS. SUMMARY OF AVERAGE ANALYSES. SAMPLE NO. 2. OAK BARK.

	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Non-tannins Per cent.	Tannin Per cent.	Per cent.
Without thimble	23.53	20.49	3.04	8.69	11.80	57.59
With thimble	22.48	19.76	2.72	8.32	11.44	57.90
Difference	1.05	0.73	0.32	0.37	0.36	0.31
ABSOLUTELY DRY BASIS.						
Without thimble	24.33	21.18	3.15	8.98	12.20	
With thimble	23.24	20.44	2.80	8.60	11.84	
Difference	1.09	0.74	0.35	0.38	0.36	

The following extraction and analyses were also made by the chairman:

Digitized by Google

TABLE 13.—AIR DRY BASIS. SAMPLE NO. 1 HEMLOCK BARK. WITHOUT THIMBLE.

	Analysis No.	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Non-tannins Per cent.	Tannin Per cent.	Purity Per cent.	Moisture Per cent.
Reed extractor, 2 hrs. and 14 hrs. continuous extraction.	1	22.23	17.77	4.46	7.07	10.70	60.17	10.05
	2	21.69	17.71	3.98	6.94	10.77	60.80	10.05
	Av.	21.96	17.74	4.22	7.01	10.73	60.49	10.05
Reed extractor, 2 hrs. and 6 hrs. continuous extraction.	1	19.93	16.40	3.53	6.09	10.31	62.88	10.05
	2	19.24	15.58	3.66	5.63	9.95	63.81	10.05
	Av.	19.59	15 99	3.60	5.86	10.13	63.33	10.05
Teas extractor, 2 hrs. and 6 hrs. continuous extraction.	1	19.72	16.19	3.53	5.75	10.44	60.31	10.05

TABLE 14.—AIR DRY BASIS. SAMPLE NO. 2 OAK BARK. WITHOUT THIMBLE.

	Analysis No.	Total solids Per cent.	Soluble solids Per cent.	Insolubles Per cent.	Non-tannins Per cent.	Tannin Per cent.	Purity Per cent.	Moisture Per cent.
Reed extractor, 2 hrs. and 14 hrs. continuous extraction.		23.88	20.49	3.39	8.81	11.68	56.95	3.41
Teas extractor, 2 hrs. and 6 hrs. continuous extraction.	1	21.32	19.51	1.81	7.77	11.74	60.16	3.41
	2	21.77	19.79	1.98	7.83	11.96	60.42	3.41
	Av.	21.55	19.65	1.90	7.80	11.85	60.29	3.41
L. A. Cuthbert extracted the following:								
Teas extractor, 2 hrs. and 6 hrs. continuous extraction.		20.78	18.81	1.97	7.61	11.20	63 80	3.00

COMMENTS.

L. A. CUTHBERT:—Regarding the alundum thimbles I can't see any advantage in using them over the present Official Method providing that enough precaution is taken in analyzing a bark by the present method. My first attempt to run the hemlock bark

Digitized by Google

was practically spoiled by having to stop the extraction in order to pack cotton around the thimble to prevent the steam from escaping. It seems to me that where a number of barks had to be analyzed if the thimbles were used it would add considerably to the amount of work which had to be done.

C. R. OBERFELL, L. M. RICHESON:—This work was done strictly according to the procedure required by the Official Methods in *all details*. We use American Standard 1914 Hide Powder.

These results are of the same nature exactly as those I obtained some time ago by the use of the alundum thimble. There is a chance that the difference is caused not by any inherent fault in the use of the alundum thimble for this purpose, but in the construction of my extractors. They are of the Teas type, but the tube from which the condensate drips onto the bark projects only about ¼ in. from the body of the extractor. This may be the cause of part of the condensate running down between the wall of the extractor and the thimble and thus not passing through the bark, although I am of the opinion that under any circumstance or condition there will be part of the condensate pass in this manner which would be bound to have some effect in a straight percolation. I am merely throwing this out as a possible explanation of the difference which we obtained between the two ways of extracting.

F. H. SMALL, V. J. MLEJNEK:—The main object in working out this form and use of alundum thimble was to increase the convenience of the laboratory extraction apparatus. Anyone who uses the thimble will, I think, immediately grant that it is both a time saver and a convenience.

In operating the cotton and plate method seemed to effect a more complete extraction in the 500 cc. of percolate collected outside the extractor. Especially was this marked in the case of the hemlock bark.

CHAIRMAN:—The condensers used in this laboratory have center drip tubes and the first liquid through the extractor containing thimble was colorless due to condensation between thimble and wall of extractor. The results with and without the use of the thimble are practically the same on the oak bark, while in the

Digitized by Google

case of the hemlock the results with the thimble are materially lower. It would seem that the chief cause of difference in results is due to the fact that some of the steam is condensed between the thimble and wall of extractor and therefore does not percolate through the bark in the thimble, while without the thimble this water would pass through the bark.

Personally I can see no advantage in using the alundum thimble nor a saving of time and much prefer the regular Official Method.

In regard to the eight hour extraction compared with the Official Method the former gives good results on the oak bark, but quite low on the hemlock bark.

F. F. MARSHALL:—Owing to lack of time I was not able to complete my work and can only give results on hemlock bark.

HEMLOCK BARK.

	Air dry			Absolutely dry		
	Without thimble Per cent.	With thimble Per cent.	Difference Per cent.	Without thimble Per cent.	With thimble Per cent.	Difference Per cent.
Total solids	22.07	21.20	0.87	24.50	23.54	0.96
Soluble solids	17.71	17.09	0.62	19.66	18.98	0.68
Insolubles	4.36	4.11	0.25	4.84	4.52	0.32
Non-tannins	6.78	6.38	0.40	7.53	7.09	0.44
Tannin	10.93	10.71	0.22	12.13	11.89	0.24
Moisture	9.93	9.93	—	—	—	—

I have found the alundum thimble to be no extra convenience and my results show it to be no improvement over the present method.

SUMMARY.

CHAIRMAN:—In looking over the "Summary of Average Analyses" the extraction without the use of the thimble was more thorough in both cases than when the thimble was used, and it is evident that the thimble reduces the efficiency of the extraction. The difference is not very great but is consistent throughout each item of the analysis. Comparing the principal item, tannin, the hemlock bark yields 0.26 per cent. and the oak bark 0.29 per cent. higher results when the extraction is made without the use of the thimble.

Digitized by Google

Three of the collaborators claim the thimble to be no extra advantage in regard to convenience and one states that the results obtained by the use of the thimbles in practical work have been anything but satisfactory.

The chairman wishes to thank those collaborating in this work for their prompt and willing services.

STANDARD FORMS FOR REPORTING ANALYSES.*

By W. K. Alsop.

The following letter was sent to about 60 members; "The question as to the advisability of having standard forms for reporting analyses has been discussed at several of our annual meetings. At present considerable confusion may result from the different ways of reporting results from samples sent to several chemists for comparative work. I have been asked by the Council to collect data in reference to this subject with a view to including in our methods official or recommended forms for this purpose if it seems best.

"Will you kindly send copies of forms used, or your views as to the best method of stating results with a view to a standard form, for the following:

Leather analysis.
Liquor analysis.
New and spent bark analysis.
Extract analysis.

"The question has also been raised as to the desirability of including in our methods a standard table showing corrections necessary to be made to the barkometer readings of liquors of different densities at various temperatures in order to bring the readings to the standard temperature; 60° F. I presume this might include specific gravity, also Twaddell and Baumé degrees of extracts or heavy liquors. Kindly send me table or methods you use."

Twenty-four replies have been received. The majority of

* Report of 1914 Committee.

Digitized by Google

these answering inclosed forms as requested. Many of these are not used for public analytical work. There seems to be more uniformity in the form of reporting analyses than I had supposed to be the case.

VEGETABLE TANNED LEATHER.

Thirteen forms were received. The items reported are, in general, much the same, most of the differences being in arrangement. All include "fixed (or combined) tannin and four the "degree of tannage" (fixed tan ÷ hide substance × 100). It is thus evident that the "combined tannin" found by difference is considered a definite quantity. It is assumed to be the difference between the percentage of water, hide substance, uncombined tannin, uncombined non-tannins, ash and 100 per cent. According to the forms and in the absence of any information to the contrary, I assume the majority of those reporting make the determinations mentioned and assume the balance to make 100 per cent. to be "combined tannin." If so, in most cases this figure is not correct as any soluble mineral salts will appear in the water soluble material and also to some extent in the ash.

Four forms specify "insoluble ash" in making up the 100 per cent. This may mean that the ash is washed out, that the ash is determined in a definite volume of the water solubles solution and the ash indicated deducted from the total or perhaps the ash determined in the leather after washing it out. In a paper by J. G. Parker and M. Paul, "The Complete Analysis of Leather" (JOURNAL, 1910, pp. 305-316), they call attention to this matter and advise determining the ash in the leather after washing out solubles and also in the water soluble material.

Another complication is the fact that if a leather contains epsom salts and is dried in the usual manner for moisture not all the water of crystallization held by the salts is driven off. See paper by J. G. Parker and M. Paul, "Water of Crystallization of Magnesium, Aluminum and Sodium Sulphate When Present in Leather" (JOURNAL, 1911, p. 79). Watts Dictionary of Chemistry states that $MgSO_4\ 7H_2O$ melts at 70° C., loses $6H_2O$ after prolonged heating at 150–160° C. and all water of crystallization at about 280° C.

Digitized by Google

Judging from the forms received the following would be the most satisfactory.

LEATHER AS RECEIVED.

Moisture
Oil or grease
Insoluble ash
Hide substance (nitrogen per cent.)
Combined tannins
Uncombined tannins
Uncombined non-tannins

100.00

Total ash
Water soluble material
Degree of tannage (comb. tan. ÷ hide sub. × 100)
Weighting materials

BASIS ABSOLUTELY DRY LEATHER.
or BASIS LEATHER CONTAINING PER CENT. MOISTURE.
Hide substance
Load

One form was submitted to include chrome leather analysis. It would also answer for the ordinary tests of a sulphate chrome liquor.

Fat
Ash
Chrome (Cr_2O_3)
Chrome (fat free)
Sulphates (as H_2SO_4)
Acid (as H_2SO_4)
Proportion of acid to chrome
Aluminum oxide
Iron oxide
Calcium oxide
Hide substance
Tannin
Proportion of hide substance to tannin

EXTRACTS.

Eighteen forms received. The items are much the same, differing in arrangement. There are two rather distinct forms.

Digitized by Google

No. 1.

Specific gravity
Degrees Twaddell
Moisture
Total solids
Soluble solids
Insolubles
Non-tannins
Tannins (or soluble tannins)
Ash

No. 2.

Specific gravity	Moisture
Degrees Twaddell	Insolubles
Total solids	Non-tannins
Soluble solids	Tannins (or soluble tannins)
Ash	Total

The latter gives an opportunity to show that the analysis can be made to add to 100 per cent.

Some forms record soluble and insoluble ash and purity.

Extractive Materials—New and Spent.

There is considerable difference in the forms submitted. Two are given differing in much the same way as for extracts.

No. 1.

New Materials.

	As received	Dry basis
Moisture		
Insolubles		
Non-tannins		
Tannins		
Non-extractive		
Total		
Total extractive		
Soluble extractive		

No. 2.

Dry Basis.

Total solids (or extractive)
Soluble solids
Insolubles
Non-tannins
Tannins

Moisture
Per cent. tannins in air dry
Pounds tannins in ton air dry

Digitized by Google

The forms submitted for spent materials are practically identical. Evidently some use the same for new and spent materials.

ABSOLUTELY DRY SAMPLE.

Total solids
Soluble solids
Insolubles
Non-tannins
Tannins
Tannins on basis of air dry new material

LIQUORS.

The forms for tannery liquor analysis vary a good deal, both as to arrangement and items included. Judging from those submitted a rather complete form would be:

Barkometer degree
Total solids
Soluble solids
Insolubles
Non-tannins
Tannins
Acid (as acetic)
Purity
Tannin to 1° Barkometer
Proportion of tannin to acid
Ash

The forms that I have submitted are not proposed for adoption, but rather that the subject may be discussed and if the Association thinks advisable to recommend certain forms that a committee be appointed to select them.

If certain items are specified, it should tend to uniformity and lessen chance for misunderstanding. Perhaps also tend to more accuracy in some cases.

I am not prepared to report definitely in regard to the proposed correction table for barkometer readings.

Four printed tables were submitted, two of these are identical and the other two differ somewhat from each other and the other two. Several members remark on the difficulty of preparing such a table. Some comments are as follows: "It will probably be necessary to do considerable work in order to determine the

Digitized by Google

exact corrections which may possibly differ with different materials—in the examination of liquid extracts the density should be stated in terms of specific gravity and the Twaddell or Baumé be calculated from this."

"In regard to temperature correction tables, I have found that to be accurate they must be made for each individual plant—some years ago I made a very accurate table, but find the figures do not apply to the extract here at all. The difference is very largely due to the varying purity. I have found the same to apply to a less degree to corrections on tannery liquors."

"We have found that it is not possible to get a correction scale to work on solutions over 60° barkometer with any degree of accuracy, the character of the solutions causing a large amount of variation. We therefore, try to arrange to cool the solution to 60 deg. before taking our reading."

We undertook experiments to determine whether a satisfactory table can be made for tannery liquors. We propose to make liquors of different strengths from various materials and determine the correction necessary for each. These experiments are not completed.

LABORATORY APPARATUS FOR LEACHING EXPERIMENTS.*

By L. Balderston and W. K. Alsop.

The analysis of a tanning material does not furnish full information in regard to the character of the liquors which the material will yield when leached on a commercial scale. Stronger liquors than those used for analysis may be easily obtained with the customary forms of extraction apparatus, and these liquors add somewhat to our knowledge of the way the material will work in practice. By varying the temperature, the rate of percolation and the strength of the liquor we may learn much about the best method to use in leaching the material on a large scale.

Many points must, however, remain unsettled. If the tannin of the material in question is injured by high temperature, we may use a cool head leach, allowing the temperature to fall as the

* Read at the A. L. C. A. convention, Chicago, October 28, 1914.

Digitized by Google

liquor moves toward the head. To determine how many of the leaches should be boiled, how long a series should be used, and for how long a time the material should be leached in order to obtain the best total yield with the least expense, nothing will suffice but actual experiments with a series of leaches.

To attempt solution of some of these problems, and the additional one of the effect of the water used on the character of the liquors, we built a series of small leaches which have now been in use for 8 months and work quite satisfactorily. They are made of tin-coated copper, with a brass lid, tin-coated on the inside. The lid, which is fitted with a rubber gasket and held on by bolts with wing-nuts, has three perforations, one for the liquor to enter, one for a thermometer and one for an air-vent. A false bottom of fine copper gauze is provided, and the liquor escapes from beneath this by a brass tube, leading out at one side and up the outside of the can. (See Fig. 1).

Each leach is immersed to within an inch of the top in a vessel of water, so that its temperature can be controlled. These outer vessels are heated by gas flames, and by means of Roux regulators the temperature of each may be maintained at any desired point.

It was necessary to close the leaches, as otherwise evaporation would make it impossible to control the amount of water flowing through the series. Each connects with the next by a ground brass "lip union." They are arranged on a series of steps, so that the liquor flows from the tail leach to the head. In order to prevent imprisoned air from driving the liquor out of a leach by expanding when heated, a vent is provided, made by inserting a broken pipette through a cork fitted into one of the holes in the lid. This allows the escape of air without permitting much evaporation, and when a sudden flow of liquor comes, as often happens, it is caught and flows back.

In order to prevent siphoning from one leach to the next, thus leaving the top 3 in. of the upper one without liquor, a small vent is made in the connecting pipe at the top of the curve, into which is screwed a metal device similar to the pipette, on a smaller scale. The parts of a leach, excepting the false bottom, are shown in the cut, Fig. 1. The right hand one has the lid

Digitized by Google

removed, the better to show the arrangement of the vent and thermometer. The thermometers were specially made by the Precision Thermometer and Instrument Co. of Philadelphia. They are graduated in single degrees from 70 to 212° F. They are 18 in. long, with 9 in. below the lowest graduation. The case should be of brass, tin coated, and pointed at the bottom, so as to be the more easy to thrust into the leach.

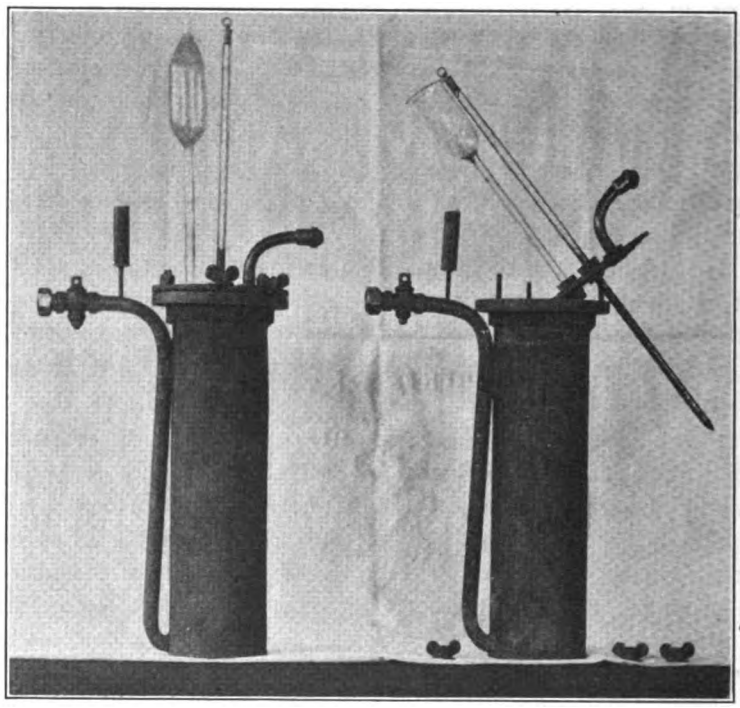


Fig. 1.

When it is desired to insert a new leach, the stopcocks are closed, the unions unscrewed and the tail leach lifted out. The others are then stepped up and the new leach put in at the bottom. The water jackets are equipped with constant level apparatus, the overflow from the tail leach passing to the next and so on. The overflow from the head leach passes to a jacket surrounding the vessel into which the liquor flows from the head

Digitized by Google

leach, so as to keep the liquor warm and avoid the deposit of reds in the receiver. The whole arrangement is well shown in Fig. 2.

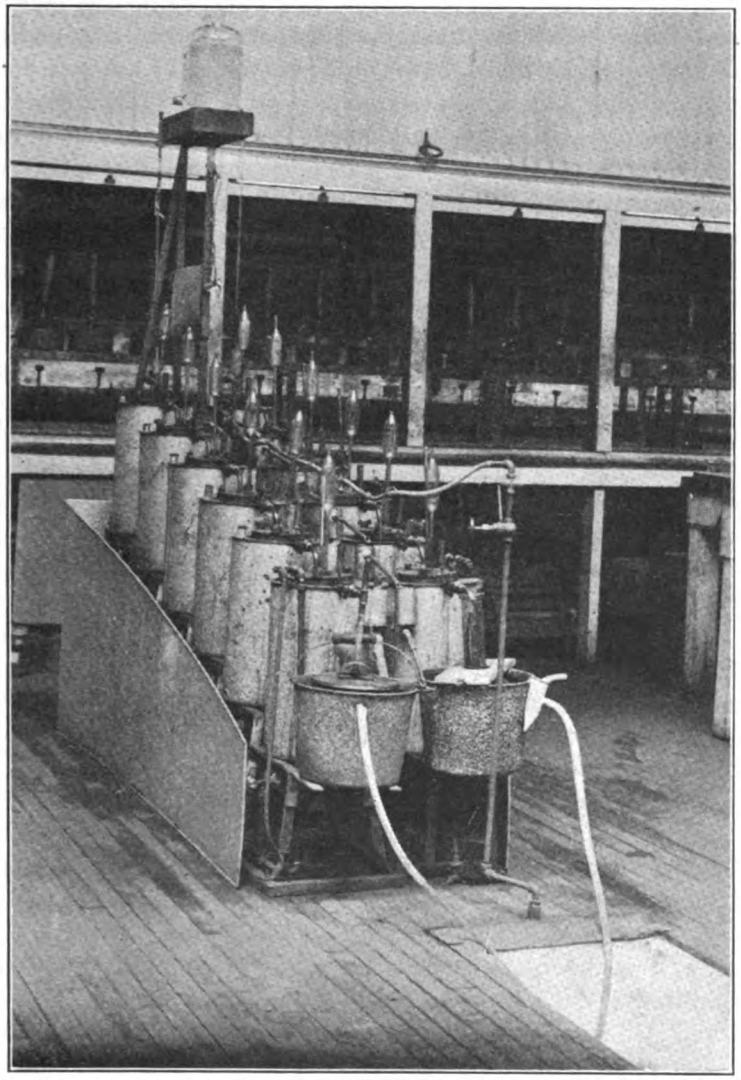


Fig. 2.

in which two sets of leaches are arranged side by side. The pipe coming up through the floor in the foreground supplies

Digitized by Google

water to the water jackets. In this picture only one of the leaches on the nearer side has a gas regulator.

The leaches are relatively narrow and deep, so that as liquor flows through them as little mixing as possible may take place. The dimensions of those shown in the cut (Fig. 1) are 4 in. internal diameter and 15 in. deep, holding 3 liters. With a charge of 700 grams of hemlock bark, these leaches yield about a 16 deg. liquor when 3 liters of water are passed through. A second set of larger leaches was made so that stronger liquors might be obtained without cutting down the amount of liquor below 2 liters. These are 7 in. in diameter at the top, tapering to 6½ at the bottom and 16 in. deep. They hold 11 liters. The taper makes it much easier to empty out the spent materials and the smaller ones should have been made in the same way. The larger leaches hold 3 kilograms of oak bark, and with 5 liters of water passed over yield about a 40 deg. liquor.

We had difficulty at first in regulating the water supply to the leaches. It must be run on in a fairly uniform stream or else put on in equal portions at equal intervals. We decided that apparatus to pour the water on in portions would be difficult to arrange, and so attempted to provide a supply dropped in through a glass stopcock. This did not work, as small temperature changes altered the setting of the cock. The plan finally adopted uses a glass jet inserted in a rubber tube leading from an aspirator bottle some 3 ft. above the tail leach. The object of placing the supply high above the jet is to keep the pressure at the jet nearly constant.

Efforts to make suitable jets were at first discouraging. The following method will give a jet delivering any required number of cubic centimeters per minute from 2 to 10 with a half hour's work. Heat in the middle a piece of glass tubing about 6 in. long, 3/16 in. internal diameter and 1/16 in. wall, until it closes. Then draw it out a little, so as to make a taper not much more than an inch long from the smallest part to full size. Cut as near as possible to the point where the bore tapers out to nothing. Then by rubbing the tip on an oil stone, testing the rate of flow frequently, the required size is soon reached.

In order to prevent the jet from clogging, the water must be

Digitized by Google

filtered and the vessel covered to keep out dust. If it gets clogged, the obstruction may usually be forced out backward by water pressure.

We drain off all the liquid possible from the tail leach which has been taken out, and pour it as rapidly as convenient on to the new tail. Then we add enough to complete the flooding of the new head to the amount of liquor desired and with a small allowance added to take care of the evaporation, put the sum of these into the aspirator bottle. After a little practice one can regulate the amount of liquor in a run within 100 grams. If it is a little short, it is very easy to push over a little from the head leach. We run on cold water from the aspirator bottle, as the stream is so small that it heats up as fast as it enters.

We have found that the leaches work best when the material is rather coarse, about like that ground in an ordinary bark mill, as very fine material does not permit a free flow of liquor. It is necessary to wet valonia before putting it into the leach, as it swells so much that if put in dry it plugs the leach, entirely preventing the liquor from passing.

Our first experiment was aimed at determining the effect of different waters on the character of liquors. We tried distilled water and three natural waters under identical conditions. The liquors were practically identical except for the small addition to the solids due to those from the water. Analyses of the 3 waters showed the following figures in parts per million:

Source	Total solids	Temporary hardness	Salt
Laboratory	64	35	12
Tannery A	235	120	42
Tannery B	346	124	201

SULPHITE-CELLULOSE BLENDS.*

By W. H. Dickerson.

Mr. Chairman and Gentlemen:—This is not a paper, but is simply a collection of a few notes that have accumulated in some of our work on cellulose extract. Naturally the experiments which I have carried on have to do more particularly with the extract with which I am more familiar.

* Delivered at the Atlantic City Convention, A. L. C. A., Dec., 1913.

Digitized by Google

The blending of sulphite cellulose extracts with various other tanning materials has attracted considerable attention, and there has been more or less written on that subject, and one of the first things that attracted my attention, as well as others who have worked with it, was the blending of sulphite cellulose extract with quebracho, and the effects of acids upon such blending. I have had various analyses made and work done by various chemists at different times, and what I am going to offer here is simply some of their work, done at my request.

The first set of analyses which we made were as follows:

ORDINARY QUEBRACHO.

	Official	½ per cent. acetic acid
Moisture	69.20	69.20
Total solids	30.80	30.80
Soluble solids	28.44	28.44
Non-tannins	1.92	3.37
Tannins	26.52	25.07
Insolubles	2.36	2.36

CELLULOSE EXTRACT.

Gravity	1.268	1.268
Twaddell	53.60	53.60
Moisture	49.43	49.43
Total solids	50.57	50.57
Soluble solids	50.50	50.50
Non-tannins	20.90	17.25
Tannins	29.60	33.25
Insolubles	0.07	0.07

50 PER CENT. ORDINARY QUEBRACHO AND 50 PER CENT CELLULOSE EXTRACT.

Moisture	59.47	59.47
Total solids	40.53	40.53
Soluble solids	40.40	40.40
Non-tannins	12.19	10.27
Tannins	28.21	30.13
Insolubles	0.13	0.13

In the above analyses the ½ per cent. acetic acid was added to the solution just before shaking out with hide powder.

Following this a more extensive series of experiments and analyses were undertaken, with the following results:

Digitized by Google

CELLULOSE EXTRACT ALONE.

	Official	0.1 per cent. acetic	0.25 per cent. acetic	0.5 per cent. acetic
Total solids	49.67	49.67	49.67	49.67
Soluble solids	49.67	49.67	49.67	49.67
Insolubles	0.00	0.00	0.00	0.00
Non-tannins	23.83	22.66	22.43	21.70
Tannins	25.84	27.01	27.24	27.97

CHESTNUT EXTRACT ALONE.

Total solids	40.16	40.16	40.16	40.16
Soluble solids	39.74	39.74	39.74	39.74
Insolubles	0.42	0.42	0.42	0.42
Non-tannins	15.02	14.90	14.79	14.79
Tannins	24.72	28.84	24.95	24.95

HEMLOCK EXTRACT ALONE.

Total solids	48.33	48.33	48.33	48.33
Soluble solids	45.42	45.42	45.42	45.42
Insolubles	2.91	2.91	2.91	2.91
Non-tannins	17.81	16.51	16.54	16.95
Tannins	27.61	28.91	28.88	28.47

ORDINARY QUEBRACHO EXTRACT ALONE.

Total solids	49.70	49.70	49.70	49.70
Soluble solids	45.50	45.50	45.50	45.50
Insolubles	4.20	4.20	4.20	4.20
Non-tannins	6.64	6.33	6.63	6.83
Tannins	38.86	39.17	38.87	38.67

CLARIFIED QUEBRACHO EXTRACT ALONE.

Total solids	43.56	43.56	43.56	43.56
Soluble solids	43.41	43.41	43.41	43.41
Insolubles	0.15	0.15	0.15	0.15
Non-tannins	5.91	5.00	6.25	6.37
Tannins	37.50	37.41	37.16	37.04

ONE-HALF CELLULOSE AND ONE-HALF CHESTNUT.

Total solids	44.48	44.48	44.48	44.48
Soluble solids	44.21	44.21	44.21	44.21
Insolubles	0.27	0.27	0.27	0.27
Non-tannins	19.95	19.36	19.30	18.62
Tannins	24.26	24.85	24.91	25.59

AVERAGE ANALYSES OF CELLULOSE EXTRACT ALONE AND CHESTNUT ALONE.

Total solids	44.91	44.91	44.91	44.91
Soluble solids	44.70	44.70	44.70	44.70
Insolubles	0.21	0.21	0.21	0.21
Non-tannins	19.42	18.78	18.61	18.24
Tannins	25.28	25.92	26.09	26.46

Digitized by Google

ONE-HALF CELLULOSE AND ONE-HALF HEMLOCK.

	Official	0.1 per cent. acetic	0.25 per cent. acetic	0.5 per cent. acetic
Total solids	48.87	48.87	48.87	48.87
Soluble solids	48.50	48.50	48.50	48.50
Insolubles	0.37	0.37	0.37	0.37
Non-tannins	24.40	23.45	22.56	21.79
Tannins	24.10	25.05	25.94	26.71

AVERAGE ANALYSES OF CELLULOSE ALONE AND HEMLOCK EXTRACT ALONE.

Total solids	49.00	49.00	49.00	49.00
Soluble solids	47.54	47.54	47.54	47.54
Insolubles	1.46	1.46	1.46	1.46
Non-tannins	20.82	19.58	19.48	19.32
Tannins	26.72	27.96	28.06	28.22

ONE-HALF CELLULOSE AND ONE-HALF ORDINARY QUEBRACHO.

Total solids	49.60	49.60	49.60	49.60
Soluble solids	49.03	39.03	49.03	39.03
Insolubles	0.57	0.57	0.57	0.57
Non-tannins	16.96	15.85	14.76	14.20
Tannins	32.07	33.18	34.27	34.83

AVERAGE ANALYSES OF CELLULOSE ALONE AND ORDINARY QUEBRACHO ALONE.

Total solids	49.63	49.63	49.63	49.63
Soluble solids	47.53	47.53	47.53	47.53
Insolubles	2.10	2.10	2.10	2.10
Non-tannins	15.23	14.49	14.53	14.26
Tannins	32.30	33.04	33.00	33.27

ONE-HALF CELLULOSE AND ONE-HALF CLARIFIED QUEBRACHO.

Total solids	46.54	46.54	46.54	46.54
Soluble solids	46.35	46.36	46.36	46.36
Insolubles	0.18	0.18	0.18	0.18
Non-tannins	15.96	14.68	14.20	13.59
Tannins	30.40	31.68	32.16	32.77

AVERAGE ANALYSES OF CELLULOSE ALONE AND CLARIFIED QUEBRACHO ALONE.

Total solids	46.61	46.61	46.61	46.61
Soluble solids	46.54	46.54	46.54	46.54
Insolubles	0.07	0.07	0.07	0.07
Non-tannins	14.87	14.33	14.34	14.03
Tannins	31.67	32.21	32.20	32.51

In the above work all acidification was made upon the solutions used for non-tannin determinations only. The reason for pursuing this course is, first, that previous tests indicated that the

Digitized by Google

loss of tannin from admixture of the extracts occurred from the increase in the non-tannin item, secondly, that the addition of the acid to the entire solution would only tend to complicate results by a possible alteration in the soluble figure and said alteration might not be paralleled in the least by naturally occurring acidity such as obtains in the tannery, thirdly, that by acidifying the solutions and not the hide powder tannery conditions are more nearly approximated, since the paramount question is what effect the souring (acidifying) of the liquors has upon the absorption of cellulose extract by the hide.

Acetic acid was selected for the acidifying agent on account of its volatility and the fact that practically all fermented tannery liquors contain it. The acid in the proportions given was added to the various solutions immediately before shaking with hide powder. In order that just comparisons might be drawn it was necessary not only to make fresh analyses of the various extracts used, alone and in conjunction with the cellulose extract, but also to make analyses of these other extracts acidified, since the effect of acidification upon the resulting non-tans might just as well manifest itself with other extracts as with the cellulose extract.

The per cent. acetic acid was calculated on the volume of solution.

As it is the usual custom in tannery practice to strengthen up liquors with extracts, it was thought that some experiments in this direction might develop some interesting facts. The first series of tests gave the following results:

	Fresh hemlock	Cellulose	Ord. queb. liquid
Total solids	48.10	49.66	52.52
Soluble solids	40.57	49.63	49.06
Insolubles	7.53	0.03	3.40
Non-tannins	14.14	22.87	6.71
Tannins	26.43	26.76	42.35

	Cellulose 6 g. / Bark liq. 500 cc. } In 1 l.		Cellulose 3 g. / Queb. ord. 2½ g. / Bark liq. 500 cc. } In 1 l.		Queb. ord. 5 g. / Bark liq. 500 cc. } In 1 l.	
	Actual	Calculated	Actual	Calculated	Actual	Calculated
Total solids	48.89	48.88	49.65	49.60	50.23	50.31
Soluble solids	45.58	45.10	45.26	44.96	43.50	44.82
Insolubles	3.31	3.78	4.39	4.64	6.73	5.49
Non-tannins	19.56	18.51	15.81	14.47	11.09	10.43
Tannins	26.02	26.59	29.45	30.49	32.41	34.39

Digitized by Google

In the above analyses the hemlock liquor is calculated as an extract. That is the comparison is the same as when a hemlock extract is used with the difference that the hemlock is in its original condition of extraction not having been evaporated as would be the extract. In order to insure having an absolutely fresh hemlock liquor, this was made in the laboratory by extraction of the fresh bark.

Following this some practical tannery experiments were made with blending of cellulose extracts with chestnut and oak liquors. It has been stated a number of time and analyses have been published tending to show that there is a loss of tannin when chestnut extract and cellulose extract are blended together, while the blending of a quebracho extract and a cellulose extract showed an increased tannin. It was desired to determine whether this same result would occur when the cellulose extract was blended with a chestnut liquor. To determine this two vats were made up of the following composition: One vat 65 per cent. chestnut wood extract and 35 per cent. chestnut oak bark liquor, and the other 55 per cent. chestnut extract, 30 per cent. oak bark liquor and 15 per cent. cellulose extract. The specific gravities of the liquors were such as to give as near the same gravity on the final mixture as possible. The analyses of these two vats of liquor gave the following results:

35 Per cent. Chestnut Oak Bark, 65 Per cent. Chestnut.

Barkometer	67 deg.
Total solids	17.17
Soluble solids	16.66
Insolubles	0.51
Non-tannins	7.00
Tannin	9.66
Acid as acetic by gelatin	0.84
Tannin to 1° barkometer	0.144
Purity	56.3

30 Per cent. Chestnut Oak Bark, 55 Per cent. Chestnut, 15 Per cent. Cellulose.

Barkometer	72 deg.
Total solids	17.28
Soluble solids	17.17
Insolubles	0.11
Non-tannins	7.06

Digitized by Google

Tannin	10.11
Acid as acetic by gelatin	0.84
Tannin to 1° barkometer	0.140
Purity	58.5

In the above tests there was not a loss of tannin in blending cellulose extract with chestnut liquors; but a decided gain. We have a reduction of 0.40 per cent. insolubles which appear in the tannin item, and the liquors containing the cellulose extract shows 58.5 per cent. purity as against the 56.3 per cent. purity of the chestnut liquor.

In conclusion it might be interesting to know there is a recent article in one of the trade papers that has given some very interesting matter on the effect of the mixture of lactic acid with cellulose extract, showing quite an increase in the absorption of the hide powder by the introduction of lactic acid into the liquors.

The matter of the permanent absorption by hide substance of cellulose extracts or liquors as compared with any other tannin—with quebracho for instance—I brought up for discussion at the last meeting, and I will not repeat it here because it came out in the JOURNAL, but it showed very clearly, as I said, that the cellulose liquors gave an absolutely permanently combined form of tannin with the hide substance.

It might be interesting also to show, in conclusion, the comparison between an American cellulose extract and a German cellulose extract. There were two samples of extract taken. They were marked by letters and sent to the Maschke Laboratory in Berlin. One was a very well known German cellulose extract, supposed to be the best in Germany, and the other was an American cellulose extract.

EXTRACT MARKED "H" (German Cellulose Extract).

Moisture	43.9
Total solids	56.1
Insolubles	0.0
Non-tannins	28.0
Tannins	28.1

Analyzed by the Filter Method.

Digitized by Google

EXTRACT MARKED "H" (German Cellulose Extract).

Moisture	43.9
Total solids	56.1
Insolubles	0.0
Non-tannins	39.5
Tannins	16.6

Analyzed by the International Leather Chemists Association Method.

EXTRACT MARKED "M" (Muskegon Extract).

Moisture	50.4
Total solids	49.6
Insolubles	0.0
Non-tannins	14.4
Tannins	35.2

Analyzed by the Filter Method.

EXTRACT MARKED "M" (Muskegon Extract).

Moisture	50.4
Total solids	49.6
Insolubles	0.0
Non-tannins	22.3
Tannins	27.3

Analyzed by the International Leather Chemists Association Method.

Gentlemen, I thank you for your attention, and I hope these little notes may contribute something to the information on the subject of this much discussed question of cellulose extracts.

ABSTRACTS.

Sole Leather Bleaching. F. O. SPRAGUE. *S. & L. Rep.*, Oct. 15, 1914. The usual number of vats is five, the order being either water, alkali, water, acid, water or water, alkali, acid, acid, water. The temperature of the baths is from 125° to 130° F., but the last water is sometimes run cold. The first bath removes excess tannin and some "reds," the alkali combines chemically with the reds, rendering them soluble and darkens the leather, since the compounds of tannin and alkali are dark-colored. The acid neutralizes the alkali and destroys the dark color due to it. A water between the alkali and acid washes out some of the alkali and solubilized reds, but not much. The use of this intervening water is slight, and if only 5 vats are available it should be omitted. One acid bath probably does not neutralize all the alkali in the leather, and a second is therefore desirable, but it should be weak. Some tanners suppose that sulphuric acid has a bleaching effect in itself, and put it in the oil wheel.

Digitized by Google

Analysis of bleach liquors shows that no solids are removed by the acid vats of the bleach. The solids in the acid baths after a day's bleaching are always less than the amount of acid added, so the alkali neutralized must be small in amount. This can only be accounted for by supposing that the leather takes up and retains an amount of acid greater than the amount of alkali neutralized. Sulphuric acid does not dissolve tannin, it precipitates it. The 3 kinds of alkali most used are sal soda, Wyandotte tanner's alkali and Wyandotte tanner's soda. Sal soda is sodium carbonate with 10 molecules of water of crystallization. It is 63 per cent. water. The tanner's alkali is sodium carbonate with about 10 per cent. caustic soda, and usually less than 1 per cent. of water. Wyandotte tanner's soda is sodium carbonate, without water of crystallization. A good strength for the alkali solution is ½ per cent. For a vat 9 by 5 by 5 ft., 50 lbs. of tanner's alkali or 135 lbs. of sal soda (a little more than 0.5 per cent.) are suitable quantities. The leather should be so hung on the dipping frame as to leave some room between. If the water contains permanent hardness, additional soda must be used, as a part will be converted into carbonate of lime and precipitated. Temporary hardness may cause loss of acid in the acid vat, neutralizing a part of the acid. One pound of 66° Bé. sulphuric acid is just about sufficient to neutralize 1 lb. of tanner's alkali. An ample amount to use is twice as much acid as tanner's alkali in the first bath and an amount equal to the alkali in the second. The alkali and first acid baths should be strengthened by an amount equal to about 5 per cent. of the original charge for each 50 sides bleached. The second acid need not be strengthened. The loss in solids removed from the leather by bleaching is less than is generally supposed. It should be estimated on the shipping weight of the leather. A series of analyses gives the loss as from 1.5 to 4 per cent., depending on the amount of extract drummed in and the kind of tanning material used in the last stages. The first water or waters should be pumped to the leach house each day to save the tannin. The sulphuric acid used generally contains iron in the form of a light colored precipitate of sulphate of iron. This is not soluble in the acid, but is soluble in water. It does not, however, stain the leather in the presence of acid. The reasonable objections to bleaching are two, loss of materials and injury to the leather by the acid left in it. The reasons for bleaching are to clear the grain and hinder it from cracking and to secure a uniform color. The loss of materials is small where the waters which precede the alkali are saved. That the presence of free acid in the leather tends to shorten its life is generally admitted, but exact data as to its effect are not available. English tanners still scrub the leather in order to clear the grain instead of using the soda and acid bleach. L. B.

Digitized by Google

ATTENDANCE AT THE CHICAGO MEETING, OCTOBER 28-31, 1914.

Among those present were:

V. A. Wallin.....Grand Rapids, Mich.
J. C. Smoot.....North Wilkesboro, N. C.
C. C. Smoot, III.....North Wilkesboro, N. C.
F. P. Veitch.....Washington, D. C.
J. H. Yocum.....Newark, N. J.
G. L. Adams.....Brooklyn, N. Y.
Cudworth Beye .....Chicago, Ill.
A. T. Brainerd.....Chicago, Ill.
J. C. Breithaupt.....Berlin, Canada
J. E. Breithaupt.....Berlin, Canada
W. H. Gardner.....Basic City, Va.
L. H. Elkan.....Chicago, Ill.
R. C. Jacobsen.....Chicago, Ill.
C. M. Proctor.....Boston, Mass.
F. A. Loveland.....Corry, Pa.
R. A. Lang.....Berlin, Canada
F. C. Rose.....New York, N. Y.
Sigmund Saxe .....New York, N. Y.
W. H. Stifel.....Alleghany, Pa.
H. L. Pierson.....Damascus, Va.
W. K. Alsop.....Ridgway, Pa.
C. R. Delaney.....Hanover, Pa.
W. A. Fox.....Kenosha, Wis.
T. A. Faust.....Newark, N. J.
A. W. Hoppenstedt.....Buffalo, N. Y.
H. H. Hurtt.....Covington, Va.
J. J. Kelly.....Cincinnati, O.
L. Balderston .....Ridgway, Pa.
W. H. Byron.....Mercersburg, Pa.
T. J. Mosser.....Newberry, Pa.
C. R. Oberfell.....Philadelphia, Pa.
Dr. Allen Rogers.....Brooklyn, N. Y.
J. A. Rogers.....Washington, D. C.
H. C. Reed.....Stamford, Conn.
A. C. Orthmann.....Milwaukee, Wis.
F. O. Sprague.....Olean, N. Y.
W. H. Teas.....Marion, Va.
Dr. Paul Voiges.....New York, N. Y.
H. T. Wilson.....Asheville, N. C.
Roy H. Wisdom.....Stamford, Conn.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. IX DECEMBER, 1914 No. 12

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $6.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1914, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, F. P. VEITCH, W. K. ALSOP, . . . Past Presidents

OFFICERS, 1914-'15

PRESIDENT—LOUIS E. LEVI, 781 Sherman Boulevard, Milwaukee, Wis.
VICE-PRESIDENT—EDWIN J. HALEY, 82 Beaver Street, New York, N. Y.
SECRETARY-TREASURER—H. C. REED, 227 Fulton Street, New York, N. Y.

COUNCIL — C. R. OBERFELL, Harrisonburg, Va.
T. A. FAUST, 323 Academy Street, Newark, N. J.
W. H. TEAS, Marion, Va.
W. A. FOX, Kenosha, Wis.

ELECTIONS.

ACTIVE

Guy T. Creese, % Creese & Cook Co., Danvers, Mass.
Harold L. Pierson, % Smethport Extract Co., Damascus, Va.
Oskar Riethof, % W. F. Mosser Co., Richwood, W. Va.
L. E. Stacy, North Wilkesboro, N. C.
Joseph Stodola, 220 33d St., Milwaukee, Wis.

ASSOCIATE.

Philip G. Kemp, 325 W. Main St., Louisville, Ky.
Paul F. Leach, 147 W. Kinzie St., Chicago, Ill.
Wm. P. Long, Pewee Valley, Ky.
F. M. Shaw, Escanaba, Mich.

CHANGE OF ADDRESS.

Roy J. Bailey, to % Dubois Laboratory Co., Dubois, Pa.

Digitized by Google

ELEVENTH ANNUAL MEETING.

The eleventh annual meeting of the American Leather Chemists Association was held at the Hotel Sherman, Chicago, October 28, 29, 30 and 31, 1914. A partial list of those present was printed in the November number, page 498. It is not possible to make a complete list, but a few additional names follow:

Harrison L. Clough, Merrimac, N. H.; J. V. R. Evans, Sheboygan, Wis.; Victor H. Kadish, Milwaukee, Wis.; Dr. Louis E. Levi, Milwaukee, Wis.; Warren S. Loud, Chicago, Ill.; Douglas McCandlish, Milwaukee, Wis.; F. H. Small, Worcester, Mass.; W. R. Cox, Chicago, Ill.; J. J. Desmond, Corry, Pa.; A. H. Gallun, Milwaukee, Wis.; E. C. Klipstein, East Orange, N. J.; A. H. Lockwood, Boston, Mass.; V. G. Lumbard, Chicago, Ill.; L. T. Roenitz, Chicago, Ill.; T. J. Shaut, Ashland, Kentucky; W. M. Spaulding, Worcester, Mass.; Joseph Stodola, Milwaukee, Wis.; George Hammond, C. E. Washburn, Albert Roth, Ann Arbor, Mich.; John E. Wilder, Chicago, Ill.; P. G. Kemp, Louisville, Ky.; Paul F. Leach, Chicago, Ill.

The first session began at 10.30 on Wednesday morning, the 28th, with President W. K. Alsop and Secretary H. C. Reed at the table.

—

PRESIDENT'S ADDRESS.

GENTLEMEN:—

At this the eleventh Annual Meeting of our Association, we assemble for the third time in this city, and for the second time in conjunction with the Annual Meeting of the National Association of Tanners.

It should be to our advantage to meet with the tanners, who are very generally our employers and to interest them as much as possible in our work as an Association, and it should also be to their advantage to become more familiar with our problems and aims which are generally pretty well discussed at the various sessions.

The titles of a number of papers to be read indicate that the subject matter should be of interest to both chemist and manufacturer, and I hope that a full discussion of the various matters brought out by the addresses will be joined in, not only by the

Digitized by Google

active members of our Association, but by the associate members and others interested who may be present. I should like to emphasize this,—that we especially desire such co-operation in the discussions, for it is only in this way that the greatest benefit can accrue to both of our Associations, by the joint meeting. Chemists are apt to be more or less in a rut and the same may also apply to the manufacturers and an exchange of ideas in relation to subjects of interest to both should be of value. It must be remembered that work of the chemist, beyond a rather narrow limit, can only progress satisfactorily with the co-operation of the employer and that this is to a great extent determined by the extent of the co-operation of the tanners among themselves. Chemists as a rule are quite willing to exchange views in reference to subjects which should be of common interest. It is true beyond question that a chemist working by himself cannot do as much for his employer as if he could meet and talk over matters with others working in the same field. There may be a few remarkable specimens who should be shut up for fear someone else would find out what they know and there is no question but that the greatest progress is made by co-operation. It should hardly be necessary to make such a statement and perhaps it is not. I am sure that there are numerous members of our Association who are willing to acknowledge that they owe much to our annual meetings and hope that this joint meeting will help the good work along.

Our Association has made a small gain in membership during the year. The support given to the JOURNAL by members is not what it should be. You should give this matter your attention and contribute more liberally to its pages. In fact this will now be necessary, as the war in Europe has affected a number of our exchanges from which we obtain considerable subject matter. It should be a comparatively easy matter for the members to supply enough matter for the JOURNAL without being dependent upon outsiders, although of course we wish to print everything of value independent of its source.

Some of our members are of the opinion that our annual meetings should be held in the spring instead of fall and early winter. They are of the opinion that better work would be done for our

Digitized by Google

committees if this work were called for during winter months instead of the summer, which is more or less interferred with by vacations. I suggest that the matter be discussed at this meeting, for if anything can be done to encourage better co-operation along the line of committee work no opportunity should be lost to take advantage of it.

—

The report of the Secretary showed 286 members, exactly evenly divided between the active and associate lists. During the year there had been 25 elections, 11 resignations and 2 deaths, a net gain of 12. The two deceased members were George D. Callender and Ogden W. Tunison. The Treasurer's report showed a balance in the treasury of $846.96.

The report of the Committee on Method of Stating Results of Leather Analysis, etc., was presented by the Chairman, W. K. Alsop. This report was published in the November JOURNAL. The reading of the report was followed by a rather long discussion, relating chiefly to the matter of temperature corrections for barkometer readings. An abstract of the discussion will appear in the JOURNAL later.

F. P. Veitch was next called on for a report of his committee on the disposal of tannery waste. It was decided, however, to postpone this report until the next day, so that it might be given in connection with two papers on the same topic, and so that the tanners might have the opportunity to hear it.

F. H. Small presented a report on qualitative tests for tanning materials. His report, with the discussion which followed, will appear in a future number of the JOURNAL.

The President next called for a report from the Committee on Methods of Analysis in connection with Beam House Procedure, Dr. Allen Rogers, Chairman. This report and discussion will be published later.

C. R. Delaney asked whether any member knew of a method for distinguishing between myrobalans and sumac. He understood that certain makers of sumac extracts were adding myrobalans, and wished to know whether there is any known method of detecting the adulteration. No information on the subject was given.

Digitized by Google

J. S. Rogers was called on for a report on determination of free sulphuric acid in leather. He said that he had brought some collodion thimbles which would be exhibited later, and expressed the opinion that Dr. Paessler's method, which involves dialysis through a collodion film, is valuable for qualitative work, and will probably be developed into a form which will be available for quantitative estimation.

J. H. Yocum mentioned the subject of holding the meetings of the Association in the spring at the time of the spring meeting of the National Association of Tanners in the East. On motion the President was directed to appoint a committee to confer with the tanners on this subject and report to a later session. J. H. Yocum and H. C. Reed were appointed. Adjourned to 2.30 P. M.

Wednesday afternoon, Oct. 28. The Association was called to order at 2.50. The first business was G. A. Kerr's paper on the "Color Valuation of Tanning Materials," read by H. C. Reed. This paper appeared in the November JOURNAL.

L. Balderston then read a paper on "Laboratory Apparatus for Leaching Experiments," which has been printed in the JOURNAL (November number). Some discussion followed the reading of this paper, several members expressing surprise that hard waters should leach bark as well as distilled water.

The next matter was the report of the Committee on Lactic Acid, Material used in the Manufacture of Chrome Leather, and Miscellaneous Methods, by the Chairman, L. Balderston. This report, and the discussion following it, will be published in a future issue.

F. A. Loveland next read his paper, published in the November JOURNAL, on the "Relation Between the Green Salted Weight and the White Weight of Various Portions of the Hide." He added that on the leather weights there was a difference of 53 per cent. between the shoulder and the bend. J. H. Yocum remarked that the temperature at which the liming process was carried on, the character of the water and the amount of lime used are factors which influence the white weight.

F. H. Small said that he had carried through a series of experiments of the same character. He found that the time of

Digitized by Google

liming had a great influence on the results. A pack limed three days showed for the bend a gain of 114, for the shoulder 122 and for the belly 106, while a pack in every respect similar and treated similarly except that it was limed longer showed a gain of 116 for the bend, 137 for the shoulder and 121 for the belly.

F. H. Small then read the report of the Committee on Extraction, published in the November JOURNAL. The consensus of opinion among the collaborators was against the use of the alundum thimble for the extraction of tannin materials. It having been suggested that the thimble might be an advantage in carrying out the determination of water soluble matter in leather, C. C. Smoot, III said that he had done some work along this line which promises well, and had hoped to be able to make some report on it at this time. He expects to be able to make such a report in the near future.

C. R. Delaney was called on for the report of the Committee on the Official Method of Tannin Analysis. He stated that 13 reports had been received from collaborators, but so late as to prevent him from getting his report in shape. An abstract of the discussion will be printed with the report when it is ready.

C. R. Oberfell now gave the report of the Committee on Oils and Fats, published elsewhere in this issue. Then adjourned to Thursday morning.

The third session came to order at 10.10 on the morning of Thursday, Oct. 29. The first business was the report of the Committee on Moellons, Hard Greases, Hydrogenated Oils, etc., by the Chairman, T. A. Faust, printed elsewhere in this issue.

Dr. Allen Rogers next read a paper on the "Dyestuff Situation in America," which appears in this number of the JOURNAL.

A paper on "Leach House Efficiency," by J. H. Yocum followed. This paper and the discussion which followed it will be published later.

W. K. Alsop then read the paper on "Determination of Insolubles in the Analysis of Tannin Extracts," which was printed in the November JOURNAL. A rather long discussion followed, an abstract of which will be published later.

Adjournment till 2.30 P. M. was then taken.

Digitized by Google

During the noon recess a luncheon was served to the members in a nearby room.

The fourth session began at 2.45 P. M., Thursday, October 29. J. S. Rogers illustrated the Paessler method of estimating sulphuric acid in leather. He showed two collodion thimbles, made by permitting some collodion to dry on the surface of a large test-tube and then detaching the film from the tube. The collodion is prepared by dissolving "snowy cotton," a photographic cotton, in alcohol and ether to a thick solution. The solution is poured from the flask into a wide test tube and then slowly poured back. After the film on the tube has become dry, it is well to repeat the process, so as to get a thicker film, or even sometimes to do it three times. When the film is so dry that the finger does not stick to it, the tube may be placed in a stream of water under a faucet and the film removed. The thimble so formed is a semi-permeable membrane, permitting the passage of mineral acids and salts but not of colloids and other organic substances of high molecular weight.

Mr. Rogers placed in one of the two thimbles a sample of ground leather free from acid, and in the other a similarly prepared sample of a leather containing more than ½ per cent. of free acid. The thimbles were then immersed in water containing Congo red. In a short time the one containing acid showed the characteristic change of color, while the other remained without change all the afternoon.

The next business was a paper by J. S. Rogers on the detection of oak in extracts and leathers, printed elsewhere in this issue.

F. P. Veitch then presented his report as chairman of the committee on disposal of tannery wastes. This report and the discussion following will be printed later.

C. C. Smoot, III read a paper on "Sewage Disposal and the Use of Tannery Wastes," which appears in this number.

Albert Roth next presented his paper on "The Disposal of Tannery Wastes," which is also published in this issue.

Dr. Allen Rogers gave a talk on the new process of Dr. Röhm for unhairing and bating in one operation, showing a sample of goat-skin which has been treated. This is the process described in the Journal for September, 1913, pages 408-9. A summary

Digitized by Google

of Dr. Rogers' talk and the discussion which followed will appear later. On motion, adjourned to Friday morning.

Fifth session, Friday morning, October 30, 1914. The Secretary made a further report in regard to S. & S. 590 filter paper. He had received samples from the makers early in the year which were distributed to various members and tested. These samples were found very good. Some members have complained, however, of unsatisfactory papers received since that time. The Secretary had tested Munktell's Swedish, No. 1 F in comparison with the 590, and found no discernible difference in results. In view of the fact that the supply of 590 is liable to be shut off by the war he recommended that the matter be taken up with the view of permitting No. 1 F to be substituted for 590. He had found the No. 1 F less variable in thickness than 590.

F. P. Veitch thought it might be worth while for the Association to set limits to the thickness and weight of paper suitable for this work. The limits need not be very narrow, but such a provision would probably tend toward uniformity of results.

H. C. Reed expressed the opinion that it is customary on the part of most analysts to throw out heavy papers, but there is no obligation to do this.

In answer to a question, F. P. Veitch said that an expert can sort such papers for thickness by feel, and sorting would be necessary in order to get anything like uniformity of thickness, because the papers are hand made.

H. C. Reed said he was surprised to find such concordance between results with 590 and 1 F, because a similar test some 10 years ago showed a marked difference between the two.

T. J. Mosser said that he had found a difference in insolubles in a chestnut extract of from 0.2 to 0.25 per cent. due to difference in thickness of the filter.

The next item on the program was a paper by Sigmund Saxe on "Spruce Extract." This paper, with abstract of the brief discussion which followed, will be printed later.

F. P. Veitch was called on for a paper by himself and J. S. Rogers on "The Clarification of Leather Extracts for the Determination of Reducing Sugars." This paper was published in the October JOURNAL, and Mr. Veitch therefore gave only a brief

Digitized by Google

review of results. It was suggested that the Munson and Walker table be printed in the pamphlet of methods.

S. Saxe asked for information in regard to a new product for the clarification of extracts, called Edamin. After some verbal fencing on the part of several members, bringing out no information whatever, the matter was dropped.

C. R. Delaney expressed the opinion that the Association should set a limit of variation in the case of the analysis of the same material by two chemists, so that if they differed by a greater amount some further action should be taken. In the sugar industry, he stated, such a limit is in force.

C. R. Oberfell said he believed that the International Association specify that analyses of liquid extracts must agree within 0.6 per cent. and of solid extracts within 1.5 per cent. He believed it would be well for the Association say officially what can be expected of our method in the matter of agreement.

F. P. Veitch remarked that the custom of reporting analyses to two places of decimals is misleading in seeming to imply a degree of accuracy which cannot be reached. L. Balderston supported this view.

In regard to the original proposal of Mr. Delaney, a number of opinions were expressed in opposition to any official action on the part of the organization, the matter being one which concerns only the buyer and seller and which should therefore be a matter for agreement between them. Mr. Delaney's suggestion being put into the form of a motion, was lost. The matter of one or two decimal places in reporting results of analyses was brought up again by T. A. Faust. C. R. Delaney called attention to the fact that no one is obliged to use two places. On motion of F. H. Small the matter was referred to the committee on forms of report.

H. C. Reed said that the committee on the subject of meeting in the Spring had not yet met, and asked for expression of opinion on the matter of the desirability of meeting in the Spring instead of the Fall. Many members responded, and there was a fairly equal division of opinion, some favoring the proposition to change to the Spring and others believing that such a change would be a disadvantage.

Digitized by Google

A paper on "The Hydrogenation of Oils" by Victor G. Lumbard was read by Dr. Allen Rogers. This paper, with an abstract of the long discussion following, will be printed in a later issue. Adjourned to Saturday morning.

At noon the members took lunch as the guests of the Tanners' Association, about 130 persons, members of the two associations and allied trades, being present. At the conclusion of the lunch, J. E. Wilder, President of the National Association of Tanners, spoke, emphasizing the community of interest of the two associations, especially their common interest in the prosperity of the tanning school at Pratt Institute. He introduced the head of Pratt Institute, Mr. F. B. Pratt, who gave a sketch of the work of the tanning school, and expressed the desire that more young men should come to the school with a practical knowledge of tanning and with the definite prospect of returning to the industry at the close of their course. He stated that there are now several young men who have been trained at the school, and have not found places.

After the luncheon a joint meeting of the two associations was held, with President Wilder in the chair, to consider the problems of the tanning school. This meeting was sparsely attended. It was decided to increase the representation of the A. L. C. A. on the advisory committee from two to three and to endeavor to get the committee together and secure some value to the school from their joint deliberations.

The sixth session of the A. L. C. A. was held on Saturday morning, October 31. The committee on time of meeting reported that the next Spring meeting of the tanners was to be held in California. On motion it was decided to instruct the Secretary to take a mail vote of the members of the Association to learn their preference in regard to the time of year at which future meetings shall be held.

C. R. Oberfell and F. O. Sprague were appointed tellers to count the votes which had been cast for the election of officers. Their reports showed elections as follows: President, L. E. Levi; Vice-President, E. J. Haley; Secretary-Treasurer, H. C. Reed; Members of Council, W. H. Teas and W. A. Fox. A meeting

Digitized by Google

of the new council, immediately after the adjournment of the Association was announced. The eleventh annual meeting was thereupon adjourned.

WHAT CAN WE DO TO PROMOTE A BETTER UNDERSTANDING BETWEEN THE TANNERY CHEMIST AND THE TANNERY SUPERINTENDENT?

By W. R. Cox.

It has been the wish of the editor and members of the council for some time, that the JOURNAL might be made of more service to the tanning industry as regards the every-day problems which confront the tannery chemist and the tannery superintendent, and to have these problems presented through the columns of the JOURNAL for open and frank discussion.

This idea is, I believe, one which every chemist and superintendent connected with the leather industry, will at once realize has enormous possibilities, if we enter into it with the right spirit and co-operation. Some of you who read this will feel that any remarks along this line are superfluous as there exists no misunderstanding. But, that occasionally friction does exist, is a well-known fact to those who have the opportunity to hear from both sides. I am frank to state as my opinion here and now, that there is no necessity for friction between the chemist and superintendent and I will venture to state that where it does exist, it could be eradicated, providing both parties, and it must be both parties, will meet on a common ground; *viz.*, common sense, without personal feelings entering into the decision.

I feel, and so do many others, that much good could be accomplished in the tanning industry, to-day, if the tannery chemist and the tannery superintendent would both work together, give and take. Neither one of them knows it all and both of them are necessary for the success of any tannery. For any chemist to give the impression to the superintendent, that his technical training alone will make better leather than the superintendent's years of practical experience, is a mistake, for it will not and unless he does receive some assistance, and by assistance I mean

Digitized by Google

frank statements of facts from the superintendent, he will not be of much assistance in any tannery outside of regular routine work which could be done by mail for from $2 to $10 per.

As regards the tannery superintendent, he has rights and he has feelings and often, under the seeming rough exterior, as successful superintendents are not given over much to wearing white shirts and kid gloves when making good leather, you will find on the whole, the best natured set of men in any line of manufacture and those who know them as I do, will bear out this statement. You will find these men, when rightly approached, open to suggestions, we admit willing to argue, but this is a good fault and one which comes of having to take all suggestions with caution, knowing as he does, that in no line of industry can as much capital be jeopardized and business lost, as by making untried radical changes.

There is room and work, plenty of it, in every tannery for both superintendent and chemist, but the superintendent must feel and have a certain amount of assurance, that when he has furnished, which he has to do, the suggestion for the chemist to work on and, also, supplied the chemist with certain absolute facts that are not taught in any school or found in any volume of chemistry, that the chemist will not endeavor to supplant him, but should instead give of his technical knowledge, some information in plain terms so they can be grasped and understood by the superintendent, and in this way be of mutual help. If this is carried out, much good would result and mean a great up-lift to the industry at large.

The JOURNAL, as it is to-day, is of practically no interest to the tannery superintendent. He is not interested in knowing whether there is a variance of opinion as to the methods used in analyzing extracts. What he would be more interested in would be a discussion among the chemists as to how he might get a better result with the extract when he is using it and if he is a bark tanner, as to what he could do to give the natural plumping action with extract that he used to do when leaching bark, and make as good leather. (This is only a suggestion.)

Now to some of you who have read this, will come the question: How are you going to accomplish this better understand-

Digitized by Google

ing between the tannery chemist and the tannery superintendent? I do not expect to accomplish anything. That is for you who read these lines to do and you can make a good start by placing this JOURNAL in the hands of the superintendent and explain to him what is going to follow from month to month and get him interested so that he will also feel like contributing to this department, feel that he has a place in it and with you, where his remarks will be taken seriously and suggestions offered in a fair minded way. My suggestion is this; that certain facts, and by that I mean cause and effect, will be presented in the columns of the JOURNAL every month, for open discussion by superintendents and chemists, the idea being that the superintendent will feel that he can come out and state that he is doing this, or that, getting certain results, either good, bad or indifferent, and for the chemist then to be willing to offer him, through these same columns, suggestions from a technical standpoint in plain terms, why and wherefor. On the other hand, it will also be possible for the chemist who has ideas, no matter how vague, to offer them for the superintendent to try, pass on and give results through the JOURNAL.

Now you will see that it will be up to you, the readers, as to whether this accomplishes anything or not. If it does not, then you alone are to blame. That there is a necessity for such a discussion is apparent to anybody who is connected with the leather trade. If the chemist hides behind his professional shell and will not meet on a common ground, or if the superintendent will read the ideas set forth in whatever may follow from month to month, and not be willing to do his share, no good will come. But, if both will meet in the right spirit, unlimited good will result.

In closing, I have only one further suggestion to offer and that is that I should like to hear the opinions of those actively connected with the leather industry, as regards to whether they consider this idea good, bad or indifferent; and that I do not consider it good policy for the editor or council, to allow this department of the JOURNAL, to be used as an advertising medium for any material furnished to the tanning trade. Nor do I think it a good idea to give different formulae. These discussions can

Digitized by Google

begin at the beam house and go along through to the finishing room. Discussions on these various operations as to what makes good results, or bad results, can be a field of research work for years and the copies of this JOURNAL would be priceless. In no industry is there so little known or written as in our own and it is time that we all begin to realize that while we may think that what we are doing is exactly right, still if we would drop our egotism for just a little while, we would find out that the other fellow was getting the same result, perhaps in not just our way, but that upon investigation, you may find his way better adapted to what you would want to do and then somewhere along the line, something that you were doing, that he could do that would be of assistance to him. Then, with the brains which we have represented by the American Leather Chemist Association, we would get technical ideas as to how we could do the things which we now do and think we are right, in another way and be right and, no doubt, save time and money.

DISPOSAL OF TANNERY WASTE.*

By Albert Roth.

INTRODUCTION.

Due to the particular offensive character of the tannery wastes, the tanner has long had to face the problem of a partial or complete purification of the waste discharge. The tanneries located in the more densely populated regions have had to face this problem in the past, while those more favorably situated have only just recently been called upon to do their share towards the preservation of the purity of our lakes and streams, and the abatement of what is in some instances a public nuisance. The marked increase in the use of surface waters as sources for public water supplies has only tended to hasten the necessity for the purification of all contaminating sewage. Commissions have been appointed and special sanitary districts created, the better to cope with the situation arising. The International Joint Com-

*Read at the Eleventh Annual Meeting of the A. L. C. A., Chicago, Ill., October 29, 1914.

Digitized by Google

mission on the Pollution of Boundary Waters is a recent example of this supervisory control.

The objection to the discharge of tannery wastes into our surface waters is two-fold: first, its effect upon the purifying power of the stream and, second, the aesthetic. The waste consists chiefly of spent lime and tannin liquors, waste wash waters, hair, dissolved and suspended solids, both organic and inorganic, and the different acids, dyes, salts and sulphites which will vary with the type of tannery. The wastes are detrimental to a stream into which they are discharged, due to their greedy absorption of oxygen, which checks the natural process of purification that goes on in a running stream. Oxygen is necessary both for the life of the organisms, to the activity of which the breaking down of the organic matter is due, and also for the oxidation of the decomposition products. This absorption of oxygen may tend very materially to increase the load on a filtration plant situated below the sewer outlet and which takes its raw water from the stream. Besides having a high oxygen absorbing power, the nature of the tannery waste makes it objectionable to the communities located below the outlet. The lime, hair, suspended organic matter and highly colored tannic acid, which forms a black precipitate with iron, can usually be traced far down the stream. The heavy deposits which form along the banks and the colored waters are in most cases the things objected to. On account of this, the communities have demanded the purification of the wastes, a satisfactory solution of which has proven very difficult.

The results obtained by the Massachusetts State Board of Health in its series of tests made on tannery wastes indicated the probable methods, by showing that a bacteriological treatment of the wastes is possible. This pioneer work has since been supplemented and several plants put into operation.

Before going into a discussion of the methods of purification it might be well to give a brief summary of the work done by the Michigan State Board of Health in studying the problem of tannery waste disposal. In the 1913 Session of the Michigan State Legislature the Monteith Bill was passed, giving to the State through the medium of the State Board of Health a certain

Digitized by Google

degree of supervisory control over public water supplies and over the discharge of sewage into the waters of the State. Among the first problems that confronted the Board was the abatement of creamery and tannery waste nuisances. Due to the willingness shown by the Wallin Leather Company of Grand Rapids to co-operate with the board in supplementing the work already done in tannery waste disposal, it was decided to put in an experimental station at the company's tannery at Mill Creek. The experimentation was carried on under the direction of the State Sanitary Engineer, Mr. Edward D. Rich, and the field work performed by the writer.[2]

During the summer of 1913 tests were made on the sedimentation of the wastes, with the aid of the discharged lime waste as a coagulant. The tests clearly indicated that this was insufficient where a fairly stable and colorless effluent was desired. The experiments were discontinued in the fall, but were resumed the following summer, July, 1914, with the addition of several units. The plant now consisted of a mixing tank, septic tank, contact filter, slate contact box and sand bed. The various wastes were first pumped to the mixing tank from the sump, into which the different sewers from the factory discharged. The quantity of lime, spent tan liquors, waste wash waters, etc., to be pumped, was first proportioned to the total flow of the factory. In this way representative sewage was obtained. The total amount mixed per day was about 1,100 gallons, which was allowed to run into the septic tank in 24 hours. The capacity of the septic tank was 1,125 gallons, which made the retention period of the sewage about 1 day. One-third to one-fourth of this period should be sufficient in any installation. The contact filter had an area of 22 square feet, with a depth of 4 feet of cinders 1 to 2 inches in size. The slate contact box consisted of a series of 24 slate, so arranged that the sewage was exposed to most of the 25 square feet of surface, on passing through the box. It was thought that the large surface of contact would change the form of the soluble colloids, and in this way assist in their ultimate removal. The sand bed had an area equal to 22 square feet and a depth of 28 inches, over 6 inches of gravel undrainage. The

[2] The writer is indebted to Professor W. C. Hoad, Professor of Sanitary Engineering, University of Michigan, for valuable suggestions given.

Digitized by Google

mean effective size of the sand was 0.28 mm. These units were kept in continuous operation during August and September, but it was found necessary to discontinue the tests in October. Regular observations were also made on the operation of the disposal works at the Michigan Tanning and Extract Company's plant, at Fremont, Mich. The Fremont tannery has a capacity of about 300 hides per day, with a total waste water flow of about 400,000 gallons per 24 hours, as determined by gaugings. The disposal works consist of a series of 7 sedimentation tanks 13 x 50 feet, 55 inches deep and 2 small continuous upward flow sand beds, with an area of 500 square feet each. Alumino-ferric is used as a coagulant to aid in the sedimentation and to discharge the color. The daily cost of treating the flow with chemical and disposing of the sludge has run as high as $15, which means a yearly expense of about $5,000 for operation only. Also no attempt is made to obtain a stable non-putrescible effluent by filtration, as the effluent from the continuous upward flow sand bed is discharged directly into the creek.

Sedimentation of Solids.

As a preliminary treatment, engineers are generally agreed that the wastes should first be put through an efficient sedimentation system, designed also for the economical handling of the large volume of sludge present in the sewage. This settling of the solids may be carried on either by plain subsidence or by sedimentation assisted by chemical precipitation or by some combination of the two.

Principles of Sedimentation.—In the design of efficient sedimentation tanks, it is the aim to duplicate as nearly as possible the results obtained in the laboratory, where the solids are allowed to settle in small glass cylinders or jars. Only a rough approximation of this is possible because of the hydraulic difficulties of handling a large flow, even where extreme care is used to distribute and still the flow in the tank. The use of separate fill and draw tanks has not proven economical in large installations. The disturbance set up in filling the tank increases the time necessary for sedimentation, as also does the emptying operation. This type of tank is not adaptable to conditions where it is desirable to utilize the head otherwise lost between the inlet

Digitized by Google

and outlet. The continuous flow tank has therefore generally been adopted, because of the better hydraulic possibilities. In this type, the velocity of the sewage in the tank is sufficiently reduced to allow for settling of the solids. Some of the more important details to be noted are as follows:

1. Inlet should be baffled. The sewage should be made to enter the sedimentation compartment at about ⅓ its depth and along its entire width. This reduces the amount of dead area in the end of the tank and also quickly and quietly reduces the velocity. As was noted at the Fremont plant, if the sewage enters the tank directly at the surface with a high initial velocity, it will flow across a large proportion of the tank before it is sufficiently stilled to allow the solids to settle. At the same time a disturbance is created at the inlet end of the tank which practically nullifies its use for sedimentation.

2. Outlet should be baffled. Preferably the sewage should be drawn off over a weir, in order to assure even distribution of the flow. A baffle at the outlet, extending down about twice the depth of the scum, will keep any floating matter from passing out over the weir. As at the inlet end, the sewage should not be allowed to rush to a single outlet pipe, and thus increase the velocity and reduce the sedimentation value of the outlet portion of the tank.

3. Retention period ample. The sedimentation compartment should be large enough to allow for sufficient storage capacity, to obtain the settling of the solids. The time required to settle the solids in a glass cylinder or jar can be used only as an indication of the probable time of settlement. Even with the best arrangements, to still and distribute the flow, only from 85 to 90 per cent. of the volume of a tank is available for sedimentation. It should also be noted that depth of settlement plays a part. The maximum flow entering will determine the minimum retention period. This variation in the flow must be taken into account, especially in the case of tannery wastes, where the maximum flow is very often from 3 to 4 times the average. The length and breadth should be so proportioned that the velocity of the sewage should at no point be sufficient to disturb the settling action. This would also tend to exclude the use of

Digitized by Google

baffles in the body of the tank, extending any distance up from the bottom or down from the top, except where they may be used to retard the drifting forward of the sludge or scum. In case baffles are used the velocity present will depend upon the available area between the top and bottom of adjacent sludge and scum baffles.

4. Ample sludge capacity with good sludge removing facilities very desirable. The large quantity of sludge in tannery wastes makes its reduction, digestion and removal an important consideration in any tanking design. These results may best be obtained by allowing ample sludge storage and by utilizing the compacting advantages of a deep tank. Special draw-off pipes will have to be used to remove at intervals the bottom few feet of compacted sludge. The gritty, stringy nature of tannery sludge makes the use of these special devices absolutely necessary. At the Mill Creek station, the septic action and sludge digestion were very marked. The sludge in the tanks at Fremont also gave marked signs of sludge digestion when allowed to remain in the tank at least 3 weeks.

Sedimentation with Aid of Chemical Coagulant.—The points just discussed will determine very largely the efficiency of sedimentation. However, it must be borne in mind that the locality will largely determine the degree of purification necessary. In some localities it may be possible to meet the objections to the unsightly conditions by removing some of the organic matter and the color by means of sedimentation with the aid of chemical precipitation. The action of the chemical is to combine with certain constituents in the wastes to form a flocculent precipitate which upon settling tends to sweep the liquid clear of any suspended matter, also discharging some color. Lime, sulphate of alumina, alumino-ferric or iron sulphate may be used as a coagulant. But when the iron compounds are used, sufficient lime should be present, or the iron may combine with the tannin to form an inky solution. The amount of chemical used may be reduced at times when it is possible to utilize the well-known precipitation effected by a mixture of the lime and tan liquors. The tests made on the wastes from the Fremont tannery showed that this action was very marked. Tests were also made on the

Digitized by Google

settled waste from the disposal works, in which it was found that with the addition of 10 grains per gallon of alum or alumino-ferric only a partial decolorization was effected, but with the addition of 20 grains per gallon, the decolorization was practically complete.

The use of chemical precipitation at the Fremont tannery serves to illustrate the results long since determined in domestic sewage disposal, namely, that chemical precipitation is not economical when ordinary shallow tanks are used, unless very cheap sludge disposal facilities are close at hand. The tests clearly showed that the mixing of the light precipitate with the large volume of tannery sludge in a shallow tank results in a very thin sludge with a high percentage of water. When the chemical was added to the raw wastes and then allowed to settle, the quantity of sludge removed from the tanks averaged 12,100 gallons per day of very thin sludge. By changing the operation, and first allowing the wastes to settle, adding the chemical, following this by additional settling, the volume of sludge removed was cut down to 4,850 gallons per day, while at the same time a higher percentage of the suspended solids was removed from the wastes. It appears, therefore, where the large volume of thin sludge cannot be disposed of readily, special efforts must be made in the design and operation of the tanks, in order to obtain a fairly compact sludge.

Sludge Disposal.

Special drying devices, sludge presses and sieves have been tried out in an effort to obtain some cheap and efficient method of removing the residual water in the sludge. The mechanical operation of these devices has proved more or less expensive. F. P. Veitch in his paper, given at the Ninth Annual Meeting of the A. L. C. A., Dec. 5, 1912, estimates the cost of sludge pressing in England, from 50 cents to $1.25 per ton of pressed cake, in the U. S. from 75 cents to $1.50. If however, a well digested, compact sludge were drawn off from the tank, these special devices may not be necessary. A short drying period on sludge beds (12 inches to 15 inches sand well underdrained) will usually put the sludge in such shape, as to allow it to be shoveled off and handled like ordinary manure. A very good example of

Digitized by Google

what is being done with the sludge problem in domestic sewage disposal, can be had at Batavia, N. Y. The sludge from the Imhoff tank at the municipal plant is very well digested, flows readily, and contains a lower percentage of water than most septic sludge. When drawn off 8 inches deep on the drying bed, it will dry in 4 days of favorable weather. Results similar to this might be possible with tannery sludge if efficiently tanked. The value of the dried sludge as a fertilizer is generally recognized by the farmers in the vicinities, which allows for ready disposal. Some revenue might also be derived from the sale of the sludge to fertilizer companies. Where no other means of disposing the dried sludge is economical, it can be used to fill in marshy or low lying land.

In a large percentage of the installations, however, sedimentation with the aid of a coagulant and the removal of the sludge, will only be a preliminary step towards the final purification of the still highly putrescible tank effluent. It is safe to say, that even after sedimentation, the wastes contain more dissolved organic matter than is present in the ordinary domestic sewage. Further treatment of the waste is therefore imperative.

Sewage Farming.

At this point it might be well to discuss the field of sewage farming as a means of final disposal of the settled tannery waste. Various methods have been followed in disposing the sewage upon the land. In the main, the available land is first subdivided according to the flow. The sewage is allowed to flood one of the divisions which is then set aside and worked over until the soil is in shape for another dose. The irrigation of sewage has been given a thorough trial in England and Germany, as a result of which several facts have been demonstrated. Naylor, in his book on "Trade Wastes," gives 5,000 gallons per acre per day as a good average rate for the irrigation of sewage. This low rate necessarily limits the use of farming to very small tanneries or requires a large acreage of land. For an example, the Wallin Leather Co.'s Mill Creek tannery has a capacity of about 400 hides per day, with a waste water flow of about 600,000 gallons per 24 hours. By farming at a rate of 5,000 gallons per acre per day, this tannery would require 120 acres of land to efficiently

Digitized by Google

take care of the flow. When this large area of land is not available, bacteriological treatment must be resorted to. An endeavor will now be made to cite some of the results obtained by the use of the more common bacteriological filters, when used to purify tannery wastes.

Filtration.

Contact Beds.—Numerous tests have shown that the contact filter cannot oxidize and nitrify tannery waste economically. The contact bed tested at Mill Creek, failed to indicate any marked improvement of the waste. An improvement would probably have resulted with the operation of the bed for a longer period. Professor Dunbar of Hamburg showed by a series of experiments that a non-putrescible but somewhat turbid filtrate could be obtained by double contact. The low efficiency of the contact bed is largely due to the limited amount of oxygen present in the bed, which proves insufficient to reduce the strong oxygen absorbing tannery sewage.

Sprinkling Filter.—If the contact with the bacterial film and aeration could work in conjunction, the activity of the bacteria and the attendant oxidation would be greatly aided. In actual operation this condition is obtained by sprinkling the sewage over the bed. The purifying action takes place as the sewage trickles through the bed. A test of the sprinkling filter was made at Gloversville, N. Y. (description in *Eng. Record*, Vol. 61, pp. 107 157, 1910). This indicated that the filter would give a fairly well nitrified but somewhat turbid effluent, when operating at a rate of 500,000–1,000,000 gallons per acre per day. The sewage tested was a combination of the tannery wastes and domestic sewage, about ¼ of the flow being manufacturing wastes. The dilution offered by the domestic sewage would tend to increase the possible rate on the filters. Tests were also made by the Massachusetts Board of Health during 1909. The conclusions drawn are given as follows: "It is evident from these experiments that the wastes from this tannery, if properly clarified, can be easily purified by trickling filters operated at rates of from 500,000 to 1,000,000 gallons per acre daily, and that a very satisfactory purification can be accomplished by intermittent filtration through sand at a rate of 20,000 gallons per acre daily, or by

Digitized by Google

refiltration of the trickling filter effluents through sand at rates of 100,000 to 150,000 gallons per acre daily." In any installation however, the inadaptability of the sprinkling filter to the particular location, the relatively large first cost and cost of operation, may make it economical to provide for the additional sand beds necessary to take the lower rates, and in this way eliminate the use of the sprinkling filter. A rough estimate of the cost of sprinkling filters might be given at $75,000 per acre. The cost of sand beds, figuring the cost of sand in place on filter at $1.25 per cubic yard, could be placed at $6,500 per acre.

Intermittent Sand Filtration.—It was recognized very early in the work of sewage purification that filtration was a means of utilizing the purifying forces in nature by making conditions suitable for their growth. It was demonstrated that the aerobic bacteria, which are the chief factors in the oxidation and nitrification of the sewage, must have a bountiful supply of oxygen in order to carry on their work. To obtain this oxygen, intermittent dosing was used on the filters. The bed is filled with oxygen at the start, as the dose of sewage passes through it, the oxygen is absorbed and utilized by the bacteria. When the oxygen in the bed is depleted the purifying action of the bacteria necessarily ceases. Hence the dosing must stop and the bed allowed to aerate and regain its supply of oxygen, before applying another dose of sewage.

The intermittent sand filtration idea resulted in various forms of sand beds, some following the bacteriological principle and others disregarding it. The upward flow sand bed has been tried out many times for the purification of trade wastes of various kinds and for city sewages, and has necessarily always failed to purify, when the flow is continuous through the bed. Where they endeavor to use the intermittent idea of dosing, is is evident that the rates must be the same as in the downward flow filter, which means that an equal area of bed is required. The large extra cost, however, of constructing the double bottom with the upward flow bed makes its use prohibitive.

As has been previously indicated, upon the condition of the bacteriological film and the supply of oxygen depends the degree of purification. It is evident, therefore, that the character of

Digitized by Google

the sewage applied to the filter largely determines the rate possible. In the operation of the Mill Creek tests, the lime and tan liquors were mixed, but no additional chemical coagulant was used to aid the sedimentation. The tank effluent was dosed on the sand bed at a rate of 158,000 gallons per acre per day during the first month. It was interesting to note that although the filtrate was still putrescible, it was clear and practically odorless on leaving the filter. A slight surface clogging was noted after two weeks operation, which was readily overcome by stirring the top layer of sand. During the second month of operation the rate was reduced to 80,000 gallons, as a result of which a clear non-putrescible filtrate was obtained. These results substantiated in the main the results obtained by the Massachusetts Board of Health, which determined that a sand bed could properly purify the clarified waste at a rate of 70,000 gallons per acre per day.

Discussion.

F. P. Veitch, referring to the statement in his report that it is not advisable to mix limes with the other tannery wastes, said that he did not refer to the lime solution, but to the undissolved lime which increases the total solids in the sludge, and interferes with its use in the manufacture of fertilizer. The value of the lime water as a precipitant he freely conceded.

In answer to a question, whether the bacterial method of purification could be applied to tannery wastes from chrome tanneries, Mr. Roth said that the important thing is that the effluent shall be slightly alkaline, and that if this condition is fulfilled the bacterial action will go on. He had no experience with residues from chrome tanneries.

V. H. Kadish said that in Milwaukee it had been found that the effluent from chrome tanneries in which limes and spent chrome liquors were mixed was practically colorless and free from suspended matter. The lime precipitates the chrome as hydroxide, and this acts as a coagulant and sweeps the suspended solids down. Even where small amounts of vegetable tan liquors are present, the decolorization is nearly complete.

Digitized by Google

SEWAGE DISPOSAL AND USE OF TANNERY WASTES.*

By C. C. Smoot, III.

The data used in this article are compiled from records obtained in operating a sole leather tannery, tanning exclusively seventy pound average packer steers, and it is not intended to be generally applicable to other plants. All products of the tannery except the finished leather will be treated as waste. All percentages given are based upon the green salted weight of the hides.

The wastes, or by-products, will be taken up in the following order:

Hair.
Fleshings—limes.
Waste liquors.
Scouring and bleaching.
Spent tanning materials.
Sewage.

The percentage of hair varies from 8 per cent. to 16 per cent. About 3 per cent. of this finds its way into the sewage, the balance being reclaimed by washing and drying. In this condition it is baled and marketed.

The percentage of fleshings removed from the hide, based on the average results obtained from 60,000 hides, is 18 per cent. All of this is available when the fleshings are rendered into grease. About 30 per cent. of grease being recovered, while the acid solution remaining is run off with the sewage. If, however, the fleshings are limed for shipment to glue factories we have found that about 8 per cent. are not suitable for this purpose. This 8 per cent. is composed largely of the fatty products removed before soaking and liming, and should be rendered into grease.

About 50 per cent. of the lime used is taken up by the hide, 25 per cent. of the remainder passes off into the sewage, the balance being used as a spent lime suitable for agricultural purposes.

* Read at the Eleventh Annual Meeting of the A. L. C. A., Chicago, October 29, 1914.

Digitized by Google

Of waste liquors there are about 75 gallons per hide each 24 hours. This is a true waste, none of which is recovered except in the treatment of the sewage.

The operations of scouring and bleaching removes about 3 per cent., which is not recovered, except in the sewage.

Spent tanning materials are used for fuel, from which 5 per cent. is recovered as ash. This ash contains from 2½ to 3 per cent. available potash and is used in connection with the spent lime and recovered tankage, to be mentioned later in the treatment of sewage, to form a compost or fertilizer.

The sewage is treated by being forced through a sedimentation basin 50 x 40 ft., with nine longitudinal partitions. The effluent is conducted by means of a central trough to the basin, where it must pass through 380 feet before emptying itself into the stream. About 80 per cent. of the total solids are retained. The total amount of material passing through this basin in 24 hours is equivalent to 823 gallons per hide worked. The amount of tankage recovered is 18½ pounds per hide worked.

After the tanks are filled they are allowed to drain until sufficiently dry to be handled well with a shovel. The tankage is then removed, piled down and covered with a layer of spent lime followed by a coat of ashes. This is repeated about three times and left to dry. When it contains about 30 per cent. moisture it is in a good commercial condition, and finds ready sale at from $2.50 to $3.00 per ton, which allows a small return over and above the cost of labor necessary in its preparation. This material has been analyzed by our State Department of Agriculture and found particularly adapted for the fertilization of fruit trees. An average analysis of this material is as follows:

	Per cent.
Moisture on original sample	30.0
Nitrogen	0.84
Lime (CaO)	46.0
Iron and aluminum ($Fe_2O_3Al_2O_3$)	5.95
Phosphoric acid (P_2O_5)	0.34
Potash (K_2O)	0.62
Sand (SiO_2)	10.78
Organic matter	33.46

We have also analyzed the effluent passing from the sedimentation basin into the stream which shows:

Digitized by Google

	Parts per million
Total solids	7,500
Soluble solids	7,400
Insolubles	100
Nitrogen	150
Organic matter	3,274
Chloride	2,465
Sulphates	836

Solution slightly colored and cloudy. Odor not offensive.

THE DETECTION OF OAK IN TANNIN EXTRACTS AND LEATHERS.

By Jerome S. Rogers.

It is frequently necessary for the leather chemist to examine leathers and tannin extracts in order to determine the tanning materials present. Sometimes leather and tanning extracts are labeled "Pure Oak" or "Oak" when little or no oak has been used in their preparation. It has long been known that the water extract from chestnut oak bark (which is the oak most largely used in America for tanning) when made slightly alkaline with ammonia shows a decided blue fluorescence.[1] In order to improve this test and render it reliable for the detection of small amounts of chestnut oak in the presence of other tanning materials these experiments have been carried out.

Solutions of water extracts of approximately analytical strength (according to the A. L. C. A. official methods of analysis) were first prepared. The tannin was removed by precipitation with lead acetate, and the excess lead was precipitated by potassium oxalate. The filtrates, which in most cases were neutral or slightly acid in reaction, were examined for fluorescence (1) by diffused sunlight, (2) by light of an inclosed electric arc: then portions were made alkaline with Na_2CO_3 and examined (3) by sunlight, and (4) by arc light.

In the preliminary experiments the following information was obtained (1) Water extracts of chestnut oak bark which when made alkaline show fluorescence by diffused sunlight, exhibit

[1] A. E. Outerbridge, Jr., (Proc. 14th meeting Amer. Soc. of Testing Materials) found that when fluorescent oils were examined by the light of an inclosed arc, the intensity of the fluorescence was greatly increased.

Digitized by Google

this property much more intensely when examined by the light of an inclosed arc. (2) Water extracts from chestnut oak bark which are neutral or slightly acid in reaction and which do not show fluorescence by diffused sunlight, exhibit this property strongly when examined by the light of an inclosed arc. (3) Photographs of the fluorescent solutions show only to a limited degree the relative amounts of the fluorescent substance present.

Examination of the photographs will show that in a few cases it is difficult to determine whether the solution is fluorescent or not. This difficulty, however, is avoided when the solutions themselves are examined.

In photographs 3 and 4 a very slight greenish-blue fluorescence could be seen with difficulty in the solutions from the red and Spanish oaks. The amount of fluorescence, however, was very slight as compared with that of the white and chestnut oaks. Chestnut wood extract also gave a very slight blue fluorescence.

Solutions or water extracts of the following materials were prepared and treated and described as above, and photographs were taken of these solutions at the time when the fluorescent tests were made.

LIST OF TANNING MATERIALS USED.

No. 1.	White oak bark	L. & P. No. 12893
No. 2.	Red oak bark	L. & P. No. 12894
No. 3.	Black oak bark	L. & P. No. 12895
No. 4.	Spanish oak bark	L. & P. No. 12898
No. 5.	Chestnut oak bark	L. & P. No. 12896
No. 6.	Hemlock bark	L. & P. No. 2052
No. 7.	Chestnut wood	L. & P. No. 2051
No. 8.	Sumac leaves	L. & P. No. 2047
No. 9.	Myrobalans	L. & P. No. 23244
No. 10.	Quebracho wood—A. O. A. C. 1905	L. & P. No. 385
No. 11.	Mangrove bark	L. & P. No. 23246
No. 12.	Valonia beard	L. & P. No. 23247
No. 13.	Cube Gambier	L. & P. No. 23150
No. 14.	Muskegon extract	L. & P. No. 20634
No. 15.	Oak bark extract	L. & P. No.
No. 16.	Hemlock extract	L. & P. No. 21479
No. 17.	Chestnut wood extract	L. & P. No. 27982
No. 18.	Sumac extract	L. & P. No. 27981
No. 19.	Myrobalans extract	L. & P. No. 23245
No. 20.	Quebracho extract	L. & P. No. 21478

Digitized by Google

Photographs Nos. 1 to 8 inclusive are described below:

No. 1. Complete list of tanning materials (slightly acid, photographed by daylight).

No. 2. Complete list of tanning materials (slightly alkaline, photographed by daylight).

No. 3. Complete list of tanning materials (slightly acid, photographed by arc light).

No. 4. Complete list of tanning materials (slightly alkaline, photographed by arc light).

No. 5. Mixtures of oak with other tanning materials.

	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
(*a*) Oak and Hemlock	100 / 0	75 / 25	50 / 50	25 / 75	10 / 90	1 / 99
(*b*) Oak and Chestnut	(With percentages varying as in (*a*)).					
(*c*) Oak and Quebracho	(With percentages varying as in (*a*)).					
(*d*) Oak and Gambier	(With percentages varying as in (*a*)).					

Slightly acid solution, photographed by arc light.

No. 6. Mixtures of oak with other tanning materials, prepared as in No. 5, except that the solutions were made slightly alkaline. These were photographed by arc light.

No. 7. Mixtures of hemlock and chestnut, hemlock and quebracho, hemlock and gambier, chestnut and quebracho, chestnut and gambier, and quebracho and gambier. The percentages used in the mixtures were:

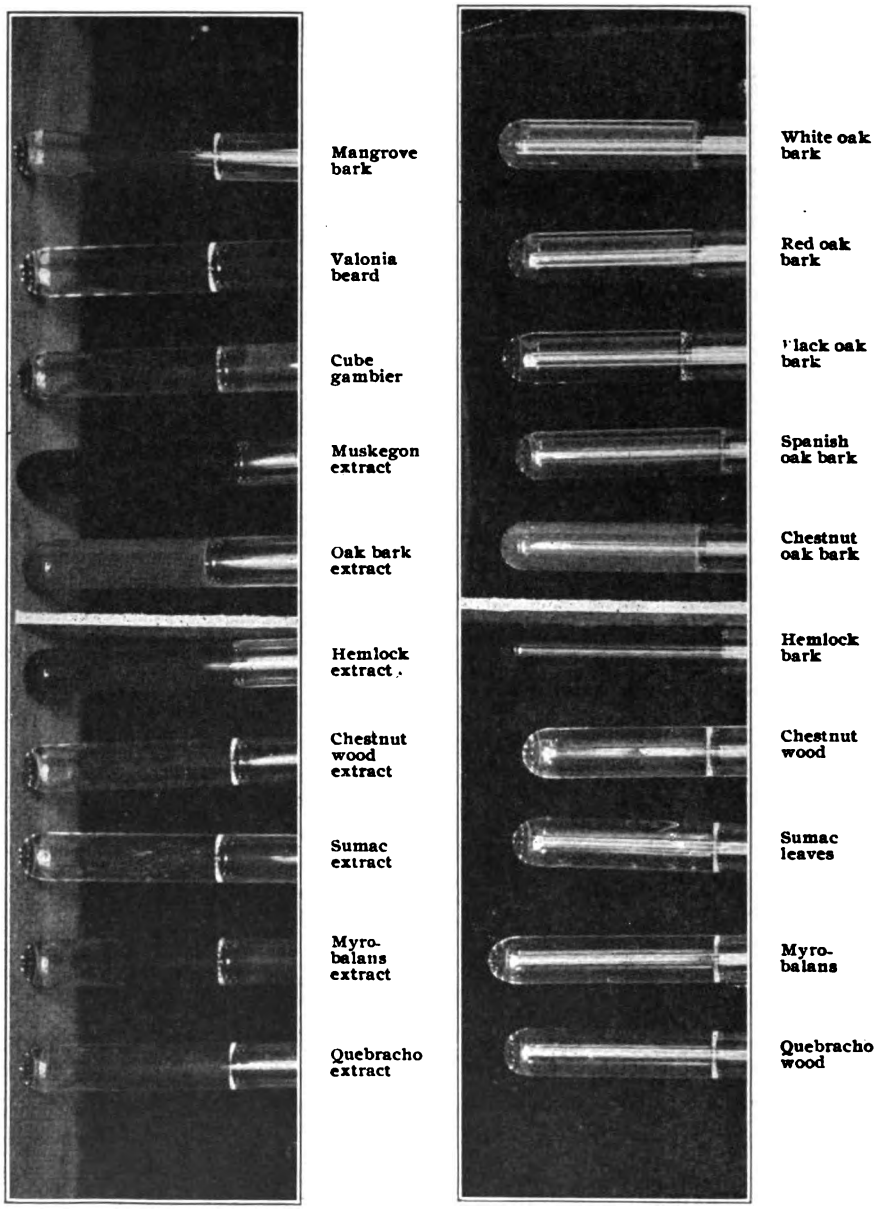
	Per cent.	Per cent.	Per cent.	Per cent.
Hemlock and Chestnut	100 / 0	75 / 25	50 / 50	25 / 75

The same percentages were used for each pair mentioned. Solutions slightly acid, photographed by arc light.

No. 8. Mixtures of materials as given in No. 7 in slightly alkaline solution, photographed by arc light.

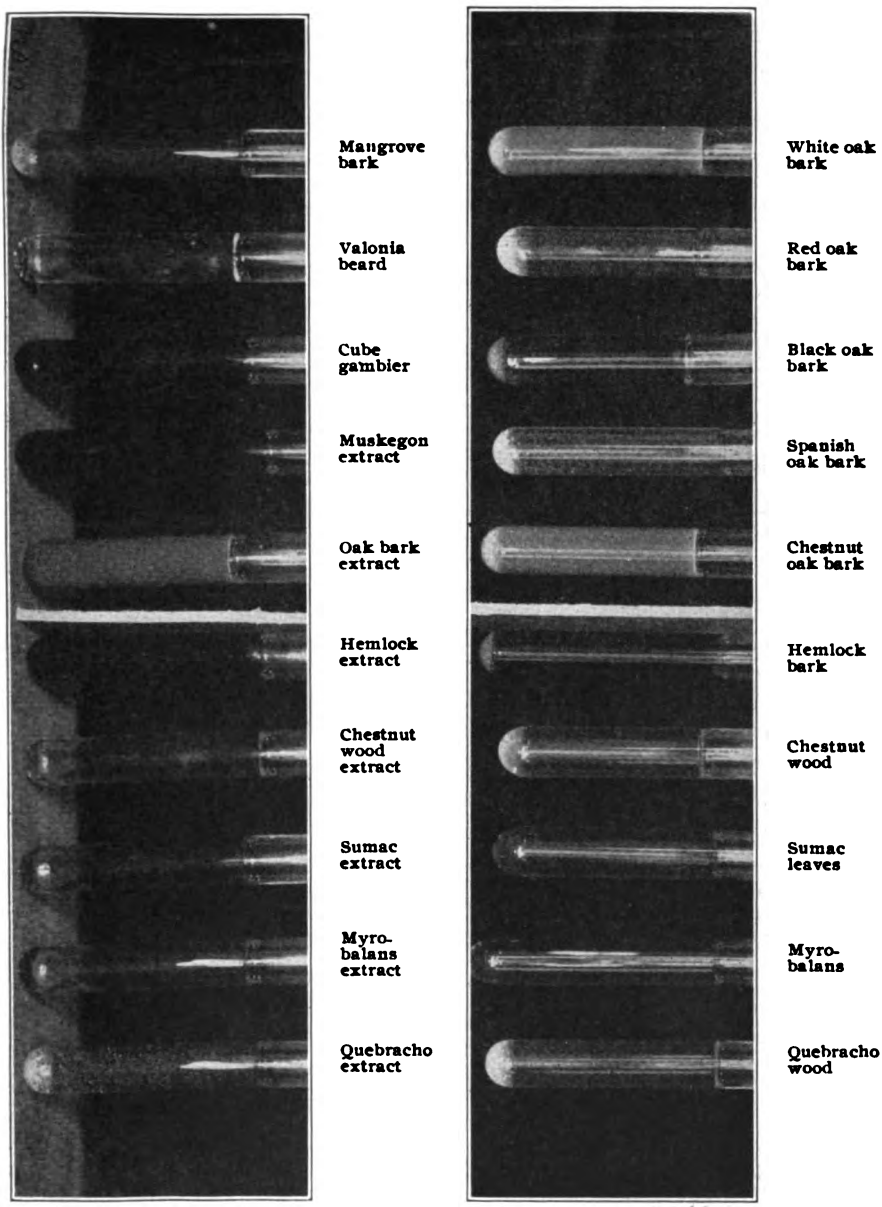
Digitized by Google

PHOTOGRAPH No. 1.—Slightly acid, photographed by daylight.



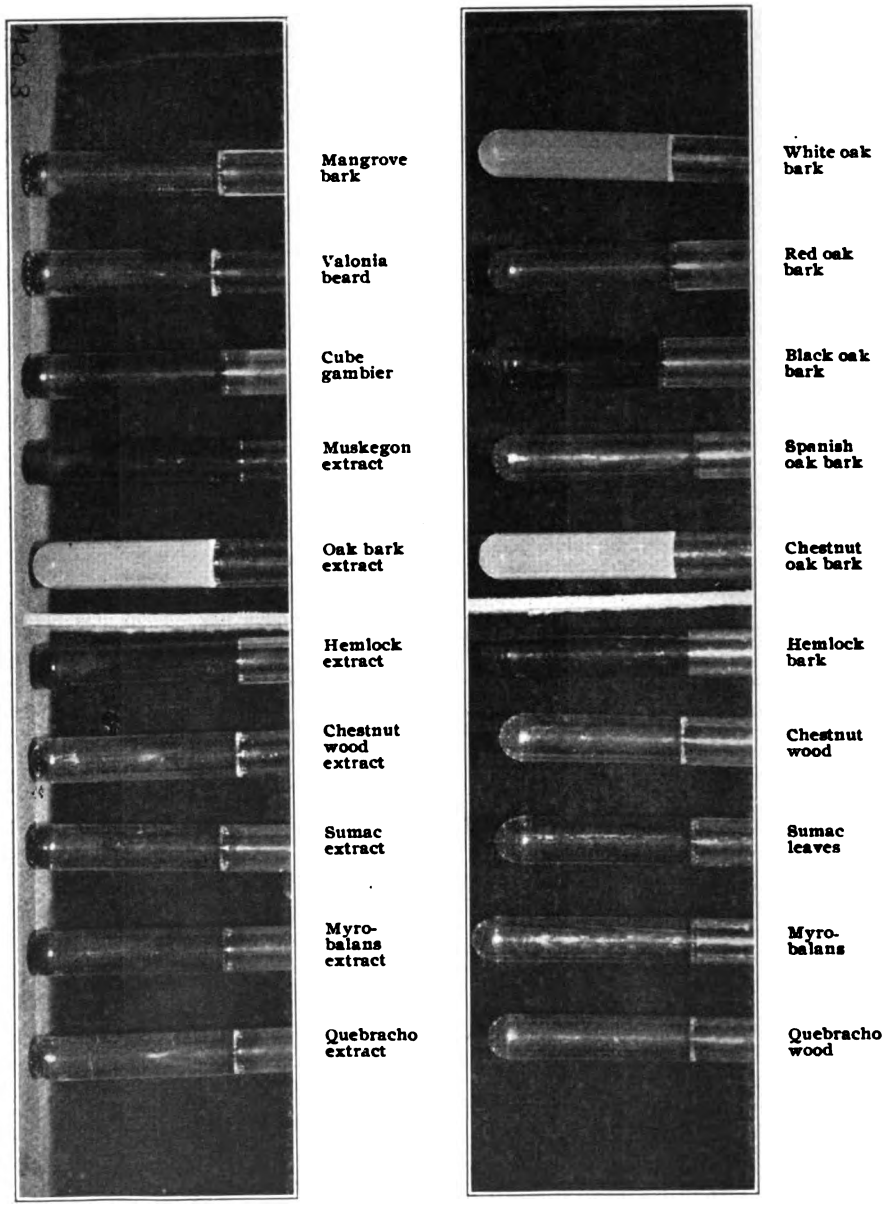
Digitized by Google

PHOTOGRAPH No. 2.—Slightly alkaline, photographed by daylight.



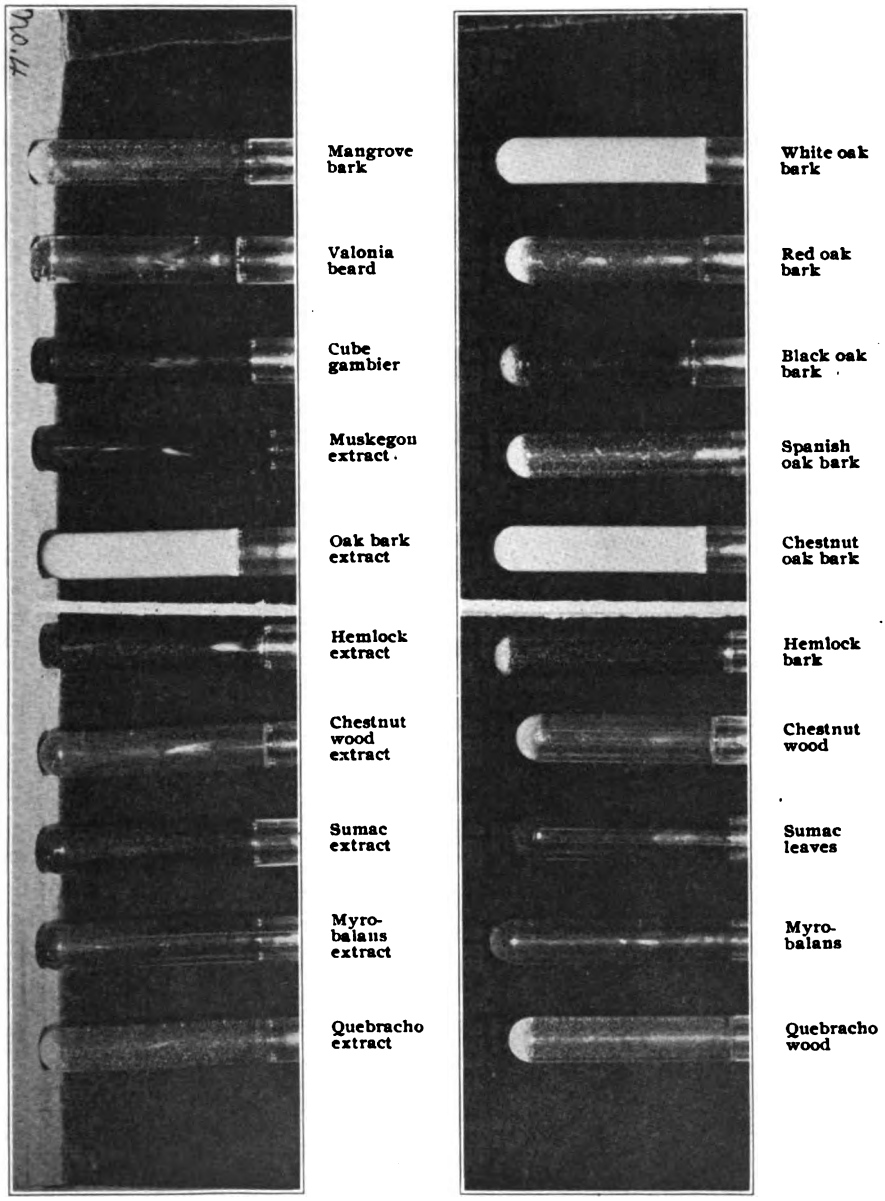
Digitized by Google

PHOTOGRAPH No. 3.—Slightly acid, photographed by arc light.



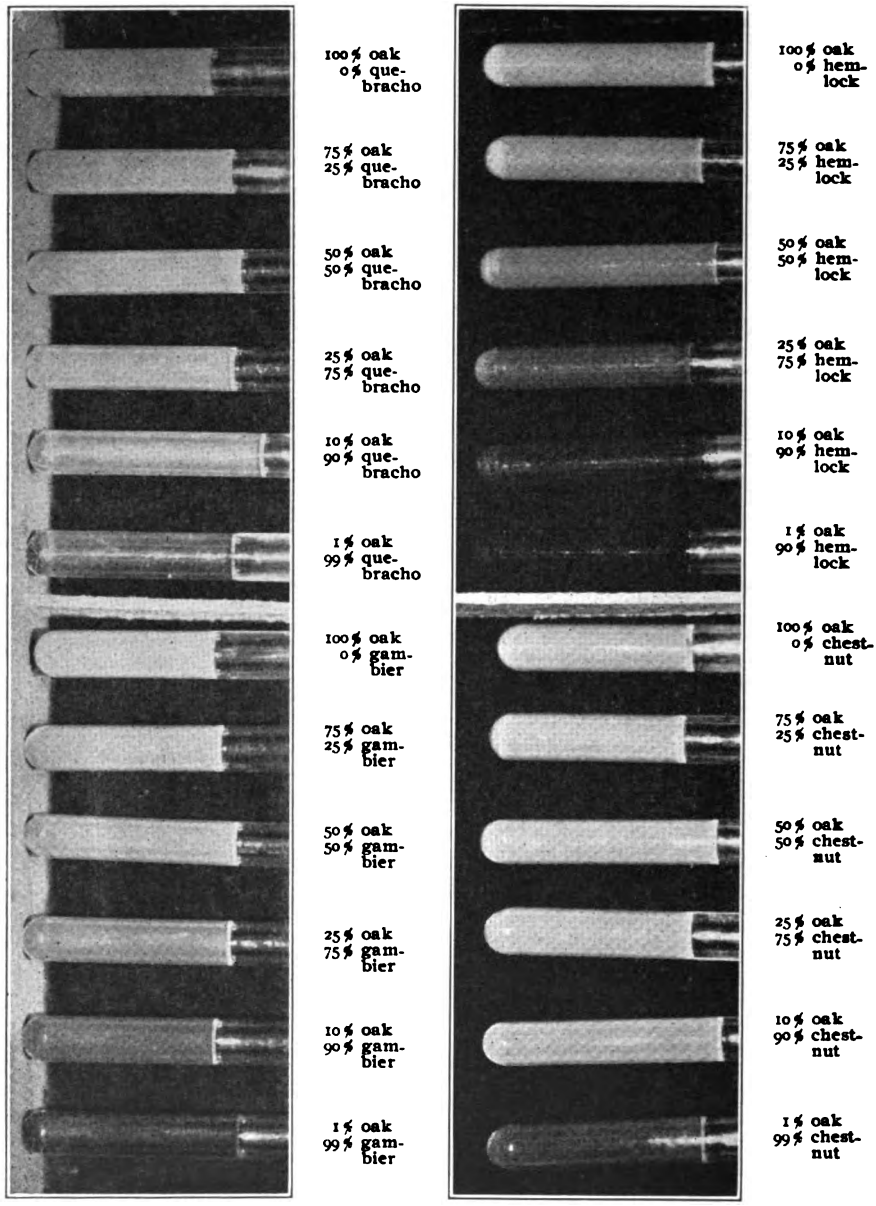
Digitized by Google

PHOTOGRAPH No. 4.—Slightly alkaline, photographed by arc light.



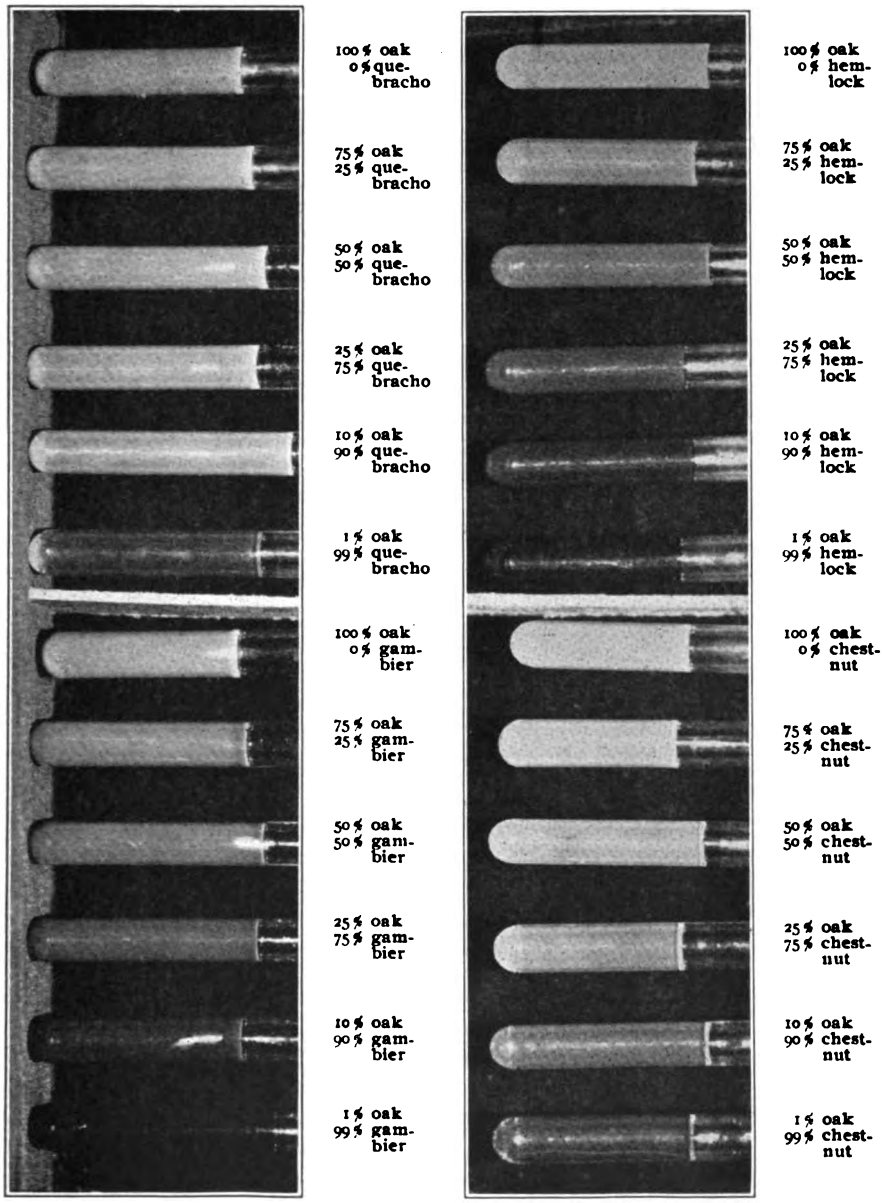
Digitized by Google

PHOTOGRAPH No. 5.—Mixtures of oak with other tanning materials. Slightly acid solution, photographed by arc light.



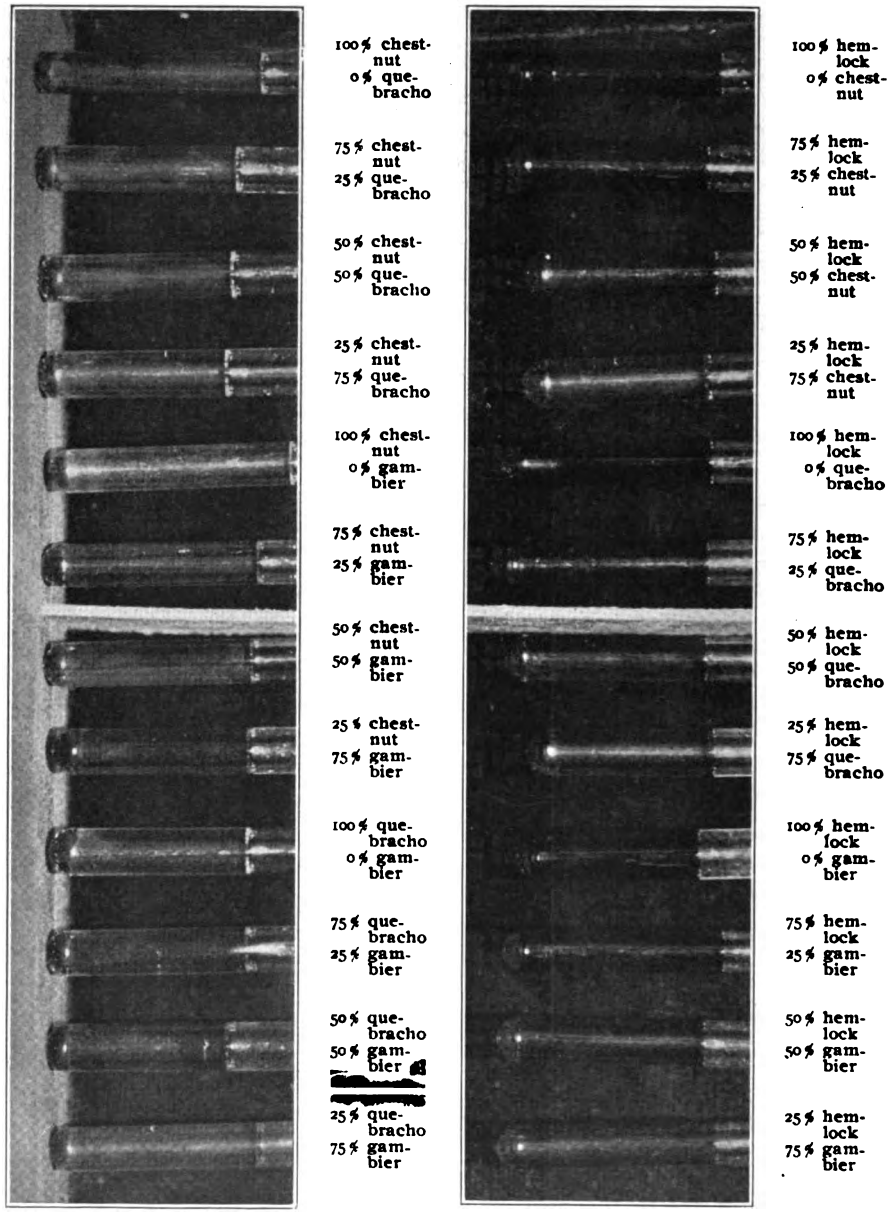
Digitized by Google

PHOTOGRAPH No. 6.—Mixtures of oak with other tanning materials, made slightly alkaline, photographed by arc light.



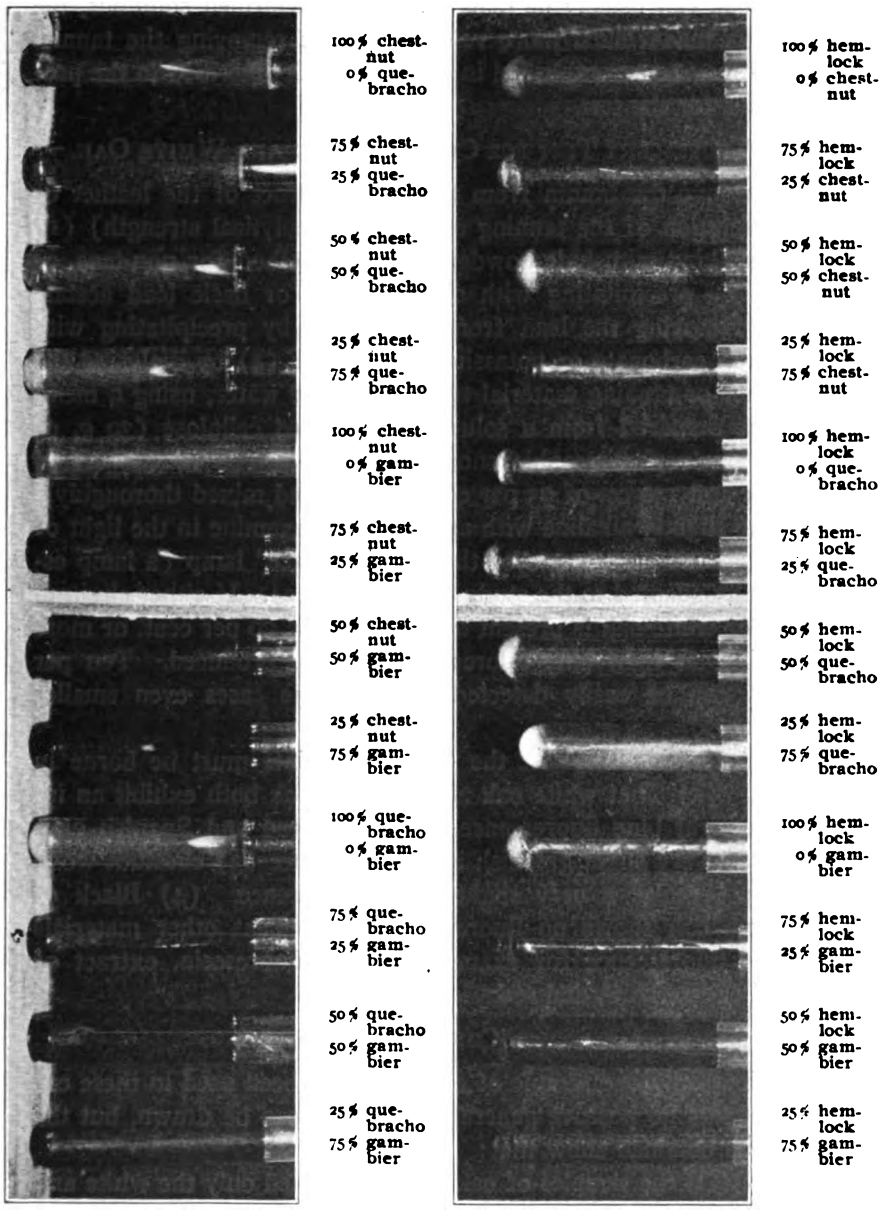
Digitized by Google

PHOTOGRAPH No. 7.—Mixtures of all tanning materials, solutions slightly acid, photographed by arc light.



Digitized by Google

PHOTOGRAPH No. 8.—Mixtures of all tanning materials, solutions slightly alkaline, photographed by arc light.



Digitized by Google

Although by use of the inclosed arc the fluorescence of chestnut oak can usually be detected in the unclarified solutions, the test is made much more reliable by first removing the tannin. This may be accomplished in three ways, as described in the procedure for the test.

Fluorescent Test for Chestnut Oak and White Oak.

Remove the tannin from the water extract of the leather or the solution of the tanning extract (of analytical strength) (1) By shaking with hide powder as in the method for non-tans, or (2) By precipitating with either normal or basic lead acetate and removing the lead from the filtrate by precipitating with sodium carbonate or potassium oxalate, or (3) by dialysing the leather or tanning material taken up in the water, using a membrane prepared from a solution of nitrated cellulose (30 g. of Anthony's photographic snowy cotton dissolved in 560 cc. of ether and 136 cc. of 95 per cent. alcohol and mixed thoroughly). Make slightly alkaline with ammonia and examine in the light of an inclosed electric arc or the "luminescence" lamp (a lamp especially adapted to the study of fluorescence). If either chestnut oak or white oak is present to the extent of 20 per cent. or more an intense light blue fluorescence will be produced. Ten per cent. can be easily detected and in some cases even smaller amounts.

In applying this test the following points must be borne in mind; (1) That white oak and chestnut oak both exhibit an intense light blue fluorescence. (2) That red and Spanish oaks show a very slight greenish blue fluorescence (3) chestnut wood extract shows a very slight blue fluorescence. (4) Black or yellow oak shows no fluorescence. (5) That other materials show fluorescence for example quinine, fluorescein, extract of wild cherry bark, and many others.

Conclusions.

Since only one sample of each kind has been used in these experiments no positive general conclusions can be drawn, but the results obtained show that:

(1) Of the samples of oak barks examined only the white and chestnut oaks exhibited intense light blue fluorescence.

Digitized by Google

(2) No other tanning material examined, with the possible exception of chestnut wood extract exhibited a fluorescence at all similar in quality or quantity to that given by white and chestnut oaks.

(3) Examination of the clarified water extracts of oak bark by means of an inclosed electric arc makes it possible to detect the presence of much smaller quantities of oak than can be detected by ordinary sunlight.

(4) In mixtures of the water extracts of chestnut oak with water extracts of hemlock, chestnut wood, quebracho, and gambier (these water extracts being of official analytical strength) one volume of the water extract from chestnut oak mixed with 9 volumes of water extract from any of the other tanning materials, that is, 10 per cent. of oak can easily be detected when examined in acid, neutral or alkaline solution by the light of an inclosed electric arc, and the fluorescence is most intense in alkaline solution.

It is realized that this test for oak leaves much to be desired; the results are presented as a contribution to the study of methods for the identification of tanning materials and it is hoped that the information included in this paper may be of aid in the interpretation of results obtained when testing for oak.

Contributed by Leather and Paper Laboratory,
Bureau of Chemistry, Washington, D. C.

Discussion.

Mr. Teas asked whether the fluorescence of oak-bark was distinguishable from that due to fluorescein. Mr. Rogers replied that the latter gives a greenish yellow fluorescence, while that of the oaks is light blue. In answer to a question by Mr. Yocum, he said that the photographs are only intended to give an approximate idea of the results. Direct observation is necessary if the method is to have practical value.

Digitized by Google

THE DYESTUFF SITUATION IN AMERICA.*

By Allen Rogers,
Pratt Institute, Brooklyn, N. Y.

Since the outbreak of hostilities in Europe the manufacturers of textiles, leather, paper and dry colors have been very much affected by the shortage of dyestuffs. Many other industries, likewise, are suffering from the lack of chemicals, which have in the past been obtained from Germany. The situation has become so serious that manufacturing associations, scientific organizations and even the public press are giving the matter a great deal of consideration. All this talk has led to more or less confusion, and the public at large have a wonderfully distorted conception of the conditions as they actually exist to-day. It is not uncommon to hear the view expressed that it is only a matter of a very short time when the products now shut off will be supplied by American manufacturers. Much as we might like to see such a thing take place, we must not be over confident of its consummation. The establishment of such an industry cannot be of mushroom growth.

Let us look for a moment at the causes which have brought Germany to a position where she controls the dyestuff and chemical markets of the world and from these facts deduce our conclusions.

The beginning of the German supremacy in the manufacture of dyestuffs dates back to the discovery of the first coal tar color "mauve" by William Henry Perkin in 1856. As will be remembered Perkin was an assistant to Prof. Hoffmann at the Royal College of Chemistry in London, and while working on the synthesis of quinine, which by the way has as yet never been made synthetically, he obtained a mass of indefinite composition which colored his towels purple. Although Hoffmann advised him to throw the muck into the sink and stick to the quinine investigation, Perkins was not satisfied until he had eventually separated a definite product which he found could be used for the dyeing of fabrics. Following this discovery, he soon isolated other colors and then tried to interest the English dyers in their

* Read at the Eleventh Annual Meeting of the A. L. C. A., Chicago, October 28, 1914.

Digitized by Google

application. In attempting to market these products Perkin did not meet with success and in fact he not only failed to arouse the interest of the English dyers, but he lost all of his money and that of his friends in the undertaking. It was not until Hoffmann had returned to Germany and established the industry there that the Englishmen awoke to the value of Perkin's great discovery. Although Perkin was then able to operate a small factory and make good some of his losses, it was too late for England to control the market which by right of discovery belonged to her.

The establishment of the coal-tar color industry in Germany also gave birth to other great chemical industries, which, under the protecting wing of the Government, have grown to such strength that she has been able to defy the competition of the entire world. The German mind, however, should be given full credit for its peculiar aptitude for scientific research. We cannot help but admire the painstaking work which has been necessary to develop such a wonderful industry. We must also admit that many of the greatest scientific discoveries have been made in the German laboratories and universities. Scientific investigation has been fostered by the Government and its application encouraged. The close co-operation between the technical schools, the university, the manufacturer and the government has resulted in a powerful combination which it is impossible to find in any other country in the world.

Should Germany lose in this conflict it would be history repeating itself, for then some other country must take her proud place and dominate the scientific world. Will that country be America? This is a difficult problem to solve as it is only a matter to be settled in the course of future events. Possibly some enlightenment may come from the information contained in the guiding maxim of the Iron Chancellor as stated by himself:

"For me there has been but one compass, one pole star after which I have steered; *Salus publica*. Since I entered public life I have often, perhaps, acted rashly and imprudently. But when I have had time for reflection I have always been guided by the question, What is most beneficial, most expedient and proper for my dynasty? so long as I was only in Prussia and nowadays for the

Digitized by Google

German nation. I have never in my life been doctrinaire. All systems by which parties are divided and bound together are of secondary moment. My first thought is of the nation, its position abroad, its independence, our organization in such a way that we may breathe freely in the world. In estimating future events we must keep an eye on the United States of America, for they may develop into a danger to Europe in economic affairs, possibly also in others at present wholly unexpected by most of us. In the future the one cannot be separated from the other. The war of the future is the economic war, the struggle for existence on a grand scale. May my successors always bear in mind and take care when the struggle comes that we are prepared for it."

The day has come and so far as Germany is concerned she was prepared, but we in America were not prepared and so as a result, we find ourselves in a predicament which becomes more serious every day. The problems confronting us deserve our most careful consideration. Although personal feelings and selfish motives may make us more or less prejudiced we must eventually be influenced by what seems to be for the best interests of the nation as a whole. What we seek is truth. Let us, therefore, put aside the personal factor and approach the problem with an open mind.

For the sake of argument I should like to put my remarks in the form of a few questions which appear to me to have a vital bearing upon the subject.

1. Have we a sufficient supply of coal tar to meet the demands of an American coal-tar color industry?

In answering this it might be of interest to note the yearly consumption of distillation products in the United States:

	Estimated use in the U. S. A. Lbs.	Tar required Gals.	Coal necessary Tons
Benzol	15,000,000	600,000,000	60,000,000
Phenol	8,000,000	160,000,000	16,000,000
Aniline	3,000,000	100,000,000	10,000,000
Naphthalene	10,000,000	14,000,000	1,430,000

The table furnished by the courtesy of Mr. S. R. Church, of the Barrett Manufacturing Co. gives us some idea of the tar required to supply even our present market. As tar contains only

Digitized by Google

about 10 per cent. of dye forming material it will be seen that something must be done with the other 90 per cent. In this country we are ahead of Europe in working up this residue so have nothing to fret about in that regard. The reason that American coal tar has not been worked up into dyestuff materials is simply because there has been no demand. Should the demand arise, there is no question but that the products could be supplied. Even if one of our great steel corporations should save the benzol they are now burning under their furnaces or allowing to escape into the air, we would have all of the benzol needed for an American coal tar industry.

2. Assuming that we have the requisite amount of coal tar; have we the necessary interlocking chemical industries to make the undertaking a success? It has been claimed that on account of the close co-operation and interdependence of the German chemical factories, what is a waste product in one becomes the raw material for another. For this reason it would appear that we could not compete. Such an argument, however, is too far fetched to warrant serious consideration. The same condition exists all over the world. That is, one factory makes certain products which are used by others, while in return the first concern purchases certain products from the latter. The interchange of products is made easy in Germany on account of short hauls, but even this is not an insurmountable difficulty. That we do not have the interlocking chemical industries is of course a fact, but what is more to the point we do not even have the main chemical industry depending upon these interlocking chemical industries.

The growth of the coal tar chemical and color industry in Germany has been slow for the reason that it has been in the making. With the knowledge, however, that we possess to-day such growth would be far more rapid.

It is not, therefore, a matter of the raw materials, neither is it a matter of the interlocking chemical industries or the slow growth of an industry that prevents us from increasing our dyestuff and chemical plants. But what we must consider most is that the manufacture of dyes and other coal tar chemicals in

Digitized by Google

Germany is a tremendous industry, controlled by a powerful combination which in this country we would call a trust.

3. Granting that we have the supply of raw materials, will it be possible for us to develop the interlocking chemical industries and the manufacture of dyestuffs in the face of these well established industries in European countries?

In discussing this question there are many problems involved, none of which can be settled by a wave of the hand. Chief among these problems is the outcome of the present struggle. Should Germany be invaded, there is little doubt that her factories would be destroyed. The industry then would be open to the world. Should she resist invasion, it then becomes a matter of finance. People who would be in a position to finance a big industry will hesitate about going into a business which is so uncertain as this is at present. When the war is over German manufacturers will be anxious to convert their stock into cash and will be very apt to do so regardless of the value of the product. This policy, which would be a death blow to any infant industry would not be a new practice by any means. What has been done in the past to crush competition will be repeated. Even at present the embargo on intermediate products is solely for the purpose of preventing American manufacturers from gaining a foothold in the dyestuff industry.

4. Will it be possible for Germany to furnish the same amount of dyestuffs when hostilities have terminated as she has in the past?

Granting that Germany is not invaded, there seems to be no doubt that she can furnish just as much material as in the past. Her research laboratories may have to be closed for the present, but her factories will no doubt continue to operate.

5. Have we a sufficient number of techincally trained men to carry on such an industry?

This question can be answered in the affirmative. We have not an army of research chemists, but under the circumstances the need is not for new colors, but for those in common use. It is probably true that we could not manufacture so economically on account of lack of experience, but a chemical compound

Digitized by Google

whether made in Germany, France, Japan or America is always the same.

6. What will our universities and technical schools do to train young men for such an industry?

The tendency of modern education is toward the industrial application of science. Many of the old line universities still hold that we should study science for science itself, but these are now in the minority. Courses in Chemical Engineering and Industrial Chemistry are springing up all over the country whose aim is to approach problems from the purely practical standpoint. More such schools are needed even though a dyestuff industry on a large scale is never established. Those that we have are here to stay and those to follow will find a hearty support. We need also more schools like Pratt Institute whose aim it is to equip young men with a technical education that will prepare them to work into positions of foremen, superintendents and heads of departments in our various manufacturing industries. Europe has been in the lead so far, but the time has come when we are beginning to see the light. As the demand increases we will find the technical schools ready and willing to meet the issue.

7. What should we do with our patent laws?

We read in nearly every paper on the present situation that our patent laws are of no help to American interests. We read always about the "working clause." It is usually claimed that we should have a working clause so that foreign patents would have to be worked in this country. As I understand it, the working clause does not make a man work his patent in some other country unless a native of said country should want to make the article. To get around this difficulty an inventor can sell a license to some one in that country. England and France have a working clause and they are in as bad a fix as we are in America. So far as our relations with Germany are concerned we have an agreement that the law does obtain in the case of American patents. This might appear at first glance that Germany has the best of the bargain as we hold no dyestuff patents in Germany while she holds many dyestuff patents here. But we must not forget that we have ten mechanical patents to one dyestuff patent which would be seriously affected by breaking this agreement.

Digitized by Google

Further than this practically all of the patents on the common dyestuffs have expired and all of the others will have expired long before we would be in a position to make them. So let us as chemists give that poor patent law a needed rest.

8. What should the government do to protect American enterprise?

This question involves more or less politics, but it is evident that if we are to have a coal tar color industry some one will have to pay the fiddler. It is true that just at the present time those who are in need of colors will promise to do anything in order to get dyestuffs, but when the normal conditions come again they will forget all about this and then buy where they can get the best figure. If we are to establish an industry of this kind there will have to be some kind of protection more effective than at present. A duty of 30 per cent. is now imposed on certain kinds of dyestuffs, while others come in free. To my own mind the suggestion that all dyes be given the same rating and an additional specific duty be added seems very wise. For example, a dye selling for 15 cents pays a duty of 4½ cents. A foreign manufacturer can pay such a duty, but suppose that he has to pay a specific tax of 5 cents per pound also? Will that cut into his profits? A specific duty would be of no value on the more expensive dyes, but then we have the *ad valorem* of 30 per cent. for the protection of the American manufacturer. The "Anti-Dumping Clause" is another very important factor in this connection.

At the present time we are making about 100 different dyestuffs in this country. These are not made in sufficient quantities, however, to satisfy the market, but it shows one thing and that is that it can be done. Of the $13,000,000 worth of coal tar colors consumed in the United States during the year 1913, $10,000,000 worth were imported and $3,000,000 worth manufactured here.

It might be said that after all the situation is not so serious as it has been painted. From the point of dyestuffs alone it may not be so serious, but the point is that a small amount of color will hold up a big industry. If we are to become interested at all in

Digitized by Google

an American Coal Tar Color Industry it is for the sole purpose of making our country self sustaining in a crisis like the present.

In all that has been written about the dyestuff situation very little has been said in regard to the importers. These men have done a service to the country which very few people realize. They have used every means possible to secure enough color to keep their customers going and have in no case advanced the prices. When the supply in stock became exhausted they used every means possible to get dyestuffs into the country in neutral bottoms. One man, Mr. H. A. Metz, has gone so far as to charter a ship with one of the other color houses, which is now on its way to Germany. This ship is sailing under the American flag and it is hoped that her mission will be successful. If this ship secures a cargo of dyestuffs it will very materially help to tide us over the present difficulty. Even this will not solve the problem, but at least these men should be given credit for what they have done.

Let us bear in mind that our textile manufacturers need dyestuffs; that our tanneries will need colors, that many other industries are directly dependent upon dyestuffs for their existence. And above all that, we have a great many more gray haired men and women in America than we did before the outbreak of the present war.

REPORT OF THE 1914 COMMITTEE ON OILS AND FATS.*

By Charles R. Oberfell.

Our provisional method for the analysis of "sulfonated oils" does not include the determination of the "neutral" or unaltered portion. This committee in 1913 tried out two procedures for unaltered oil but neither was found satisfactory, and the 1914 committee was instructed to continue this investigation.

On account of my absence from active work for some time recently I did not anticipate making any report and no collaborative work was attempted, but because of some results recently obtained I take pleasure in placing them before the Association.

* Read at the Eleventh Annual Meeting of the A. L. C. A., Chicago, October 28, 1914.

Digitized by Google

Both methods for neutral oil tried out by the 1913 committee depended on the neutralization of the sample and subsequent extraction with immiscible solvent from the soap solution. One method proposed by Lewkowitsch for the determination of the neutral portion of genuine Turkey red oil consisted in the addition of an excess of ammonia to the oil mixed with glycerol. The other method is an adaptation of the usual procedure for determining the free fatty acids in any fatty oil or grease and required the exact neutralization of the oil in alcohol solution by alkali.

The subsequent extraction in a separatory funnel with petrolic ether resulted in the formation of such emulsions as to render the methods impracticable. In the case of the Lewkowitsch method emulsions which did not break after standing 24 hours were formed, and the other method was only better in that one third the amount of oil was used in the determination.

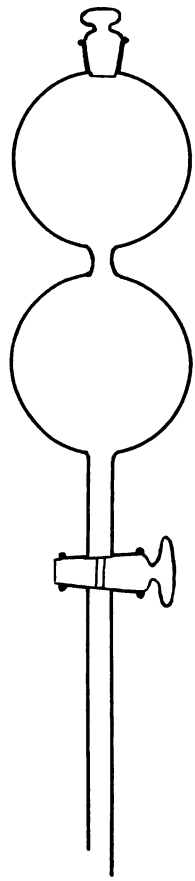
In the April issue of the *Journal* of The American Pharmaceutical Association LaWall described "A New Form of Separatory Funnel for Preventing the Formation of Emulsions in Shaking Out with Immiscible Solvents," and this apparatus I applied to the problem before us.

The apparatus consists of two bulbs separated by a very small and short neck—the one I have here I had made 6 x 6 mm., but it would work better if the opening between the bulbs was 7 or 8 mm. The bulbs can be made any size of course—this one, each bulb holds 100 cc. In one of the bulbs the liquid which is to be extracted is to be placed, adding sufficient water to completely fill the bulb. In the other the immiscible solvent which is to be used for the extraction is to be placed, completely filling the second bulb. By then inclining the bulbs at an angle, with the lighter of the two liquids in the lower bulb, the two liquids flow past each other in such a fine stream that almost complete extraction is easily accomplished by repeating the operation two or three times by inverting the funnel. There is no necessity for agitation or even rotation; in fact, it is the absence of such operations which prevents the formation of an emulsion.

The solvent may be drawn off and replaced by a fresh portion for the completion of the operation.

Digitized by Google

I have found this apparatus to be all that is claimed for it and I believe it will have a wider application in the extraction of



LAWALL SEPARATORY FUNNEL.

non-saponifiables in all oils and mixtures of oils and fats, especially moellon degras and wool-grease mixtures.

Digitized by Google

REPORT OF COMMITTEE ON MOELLON ANALYSIS.*

By T. A. Faust.

Three samples were sent out; No. 1, pure moellon, to determine methods for moisture, ash, unsaponifiables and oxidized fatty acids; No. 2, moellon containing 20 per cent. wool grease, and No. 3, moellon containing 20 per cent. wool grease and 20 per cent. mineral oil, to determine unsaponifiables only, and methods for the nature of unsaponifiables.

Sample No. 1.

Moisture.—The method of direct heating in a wide platinum dish, was suggested by the Chairman; expression of opinion as to the most reliable method was requested.

Table I shows the findings of the various members, and a remarkable agreement is evident, the greatest difference by the direct heating being less than 1 per cent. A greater variation exists in the determination made by the sand method. Consensus of opinion is in favor of direct heating in an open dish. Orthmann suggests the method of Dr. Levi, Chemist's and Tanner's Handbook, page 43, as more accurate. Alsop suggests using only 1 gram of the sample, as being quicker and sufficiently accurate.

Ash.—No ash determinations were made, but the Committee was in favor of the following proposal: "The oil remaining in the platinum dish, after the moisture is determined, shall be ashed in the usual manner, cooled and weighed."

Samples 1, 2 and 3.

Unsaponifiable.—Proposed Method: Numerous methods have been proposed for determining unsaponifiables, but the Chairman believes that the method which is now the provisional method for determining unsaponifiables in sulphonated oils, is the best, (see page 29 Official Methods), and would prevent the use of several different methods for unsaponifiables in different materials. If you do not approve of this method, give criticisms and state which method you believe is more suitable. Make the determin-

* Read at the Eleventh Annual Meeting of the A. L. C. A., Chicago October 29, 1914.

Digitized by Google

ation by this suggested method, and if you do not approve of it, make another determination by your own method. Should petroleum ether or sulphuric ether be used for extraction of the unsaponifiables?

Table No. II shows the results on the pure moellon, and Table III, on the adulterated moellons. Nearly every collaborator suggested a method different from every other one, and some suggested several, so that from a committee of 7, 8 different methods or modifications were proposed. A glance at the results as shown in Table III indicates the necessity of establishing some uniform method immediately; the results on No. 3 running from 15 per cent. to 30 per cent.

The following remarks were made by the various collaborators:

ALSOP AND CUTHBERT: I believe there should be a uniform method for unsaponifiables in all kinds of oils, but do not believe the method proposed by the Chairman quite satisfactory. On samples 2 and 3, used 50 cc. water in taking up soap, but had troublesome emulsions. Also made determinations using double the prescribed quantity of KOH, refluxing three hours, taking up with 50 cc. water; no emulsions. Using sulphuric ether instead of petroleum ether gave such persistent emulsions that it was necessary to dry the soap, before taking up with water. Sulphuric ether gives higher results, and believe it should be used.

EACHUS: Believe the method proposed, satisfactory.

ESTEN: Proposed method lacks precision. Suggest taking 5 grams sample, 2.5 grams KOH, reflux one hour, add 40 cc. water, shake out with petroleum ether three times. Claim smaller sample insures more complete saponification and is better extracted by ether; using smaller quantity of water prevents emulsions. Think relation of unsaponifiable to wool grease as definite with petroleum ether as with sulphuric ether, and in view of greater ease of manipulation, prefer petroleum ether.

ORTHMANN: Aqueous KOH not reliable, as it will not saponify all the saponifiables in wool fat. In the wet extraction, petroleum ether will not dissolve all of the unsaponifiable; sulphuric ether too tedious. In the dry extraction, sulphuric ether dissolves too much soap. Suggest the following method: 10 grams sample, (moisture removed) plus 50 cc. sodium methylate (made by

Digitized by Google

adding metallic sodium to absolute alcohol until the alcohol is saturated) reflux one hour, mix with fat-free emery, dry, powder, place in alundum thimble and extract for 24 hours with petroleum ether. This method has been found satisfactory, and is suggested for use when wool fat is suspected.

SMALL AND AMES: Think proposed method preferable to official method for unsaponifiables in oils, but suggest the use of double the amount of KOH, as the ether will separate more readily, and less difficulty with emulsions. Prefer petroleum ether to sulphuric ether.

OBERFELL: Experience has indicated that the proposed method is the most reliable.

SPRAGUE: Believe sulphuric ether should be used where wool grease is present. Do not think it necessary to evaporate the soap.

CONCLUSION.

The proposed method, judging by the remarks of the collaborators, is not satisfactory for moellons. This method was the result of the work by Oberfell's Committee on Sulphonated Oils last year, and was thought satisfactory, but the adulterated sample used in the Committee work, contained only 5 per cent. mineral oil, and did not bring out the weak points such as the sample used by this Committee.

In view of the great diversity of opinion, the Committee cannot propose a method at this time, but a careful study of the results and remarks, suggests the following compromised modification for discussion at this meeting:

Five gram sample plus 2½ grams KOH, dissolved in a little water (or 5 cc. of a 50 per cent. KOH solution), and 25 cc. alcohol, reflux one hour (use glass beads if necessary), dissolve soap in 50 cc. hot water, cool, transfer to separatory funnel, extract three times with petroleum ether (using alcohol if necessary); wash ether three times with small quantity water.

Two collaborators prefer sulphuric ether; the remainder petroleum ether.

DETERMINATION OF THE NATURE OF THE UNSAPONIFIABLE.

The members of the Committee were requested to report the

Digitized by Google

percentage of wool grease products and mineral oil in the adulterated sample, but every member dodged.

The Chairman offered the following suggestions:

If in shaking out the unsaponifiables, insoluble soaps (not broken up by alcohol) are formed, wool grease products may be suspected. To confirm, acetylate, pour into narrow tube, and note whether a magma of crystals settles out on cooling. Such crystals are generally indicative of wool grease. If no insoluble soaps are formed, and clear oil settles out in the tube, mineral oil is present. If both a magma of crystals and clear oil settle out, the crystals indicate wool grease products, and the clear oil is probably mineral oil, but may be wool grease oleine. If in doubt, determine the iodine value of this clear oil. Wool grease hydrocarbon oils have an iodine value of about 50, while the iodine value of mineral oil is generally below 20.

The following comments were made:

ESTEN: Acetylation test misleading and not reliable.

ORTHMANN: If on cooling the acetylated product, crystals settle out, wool grease may be suspected. Samples No. 2 and No. 3 showed a positive test, and insoluble soaps were noted in both samples when shaking out the unsaponifiable. Deem it necessary to first adopt a reliable method for determining unsaponifiables. Suggest determining the saponification value of the acetylated unsaponifiable.

SMALL AND AMES: Do not know of any reliable method; the suggestions of the Chairman have not given satisfactory results, although a reasonably satisfactory judgment can be found from these suggestions.

SPRAGUE: Suggest the following method: a drop of the moellon itself is dissolved in a little chloroform, acetic anhydride and a drop of sulphuric acid added; a green fluorescence indicates isocholesterol and consequently wool grease. By this test, samples 2 and 3 show wool grease.

CONCLUSIONS.

It is regretted that the method suggested by the Chairman was not investigated more thoroughly, as it is the most promising. The unsaponifiable from 10 grams sample No. 2 was acetylated, allowed to stand over night, and showed no clear oil, but a large

Digitized by Google

magma of crystals. The top portion of these crystals were those insoluble in anhydride, and resembled vaseline in appearance; the lower portion of the crystals were those which dissolved in anhydride, and settled out as a light-colored magma on cooling. There being no free oil evident, the inference is that the unsaponifiables are composed of wool grease. When petroleum ether is used, and mineral oil absent, experience has shown that the percentage of unsaponifiables multiplied by 3, gives the approximate quantity of wool grease present. In this case, by this method, finding 5.80 per cent. unsaponifiables, multiplied by 3, shows 18 per cent. wool grease.

The unsaponifiable of 10 grams of sample No. 3 was acetylated in the same manner, and on cooling showed 2.5 cc. of light clear oil on top, and a magma of crystals beneath, indicating both mineral oil and wool grease. The 2.5 cc. clear oil indicates about 25 per cent. mineral oil present; deducting this percentage from the unsaponifiable, leaves about 4 per cent. due to wool grease, or multiplying by 3, 12 per cent. wool grease.

SAMPLE 1.

Oxidized Fatty Acids.—The Chairman suggested the method by Eachus, page 240, A. L. C. A. JOURNAL, 1913.

The results as shown in Table IV, show too much variation, and while the value of this determination is doubtful. more concordant figures are desired.

Orthmann prefers the method as described in "Tanner's and Chemist's Handbook, page 44, in that it avoids any loss of oxidized fats in the acid waters. Small prefers the Lewkowitsch method, as being easier of manipulation. The remainder of the committee prefer the Eachus method. Sprague determined the oxidized fatty acids in the wash waters, and found 0.72 per cent. Most of the collaborators considered the loss in the acid waters negligible.

The Chairman believes that if the Eachus method was adhered to strictly, paying special attention to the amount of acid added, avoiding oxidation during the analysis, and guarding against any loss of oxidized fats which may adhere to the beaker, the method would be sufficiently accurate.

Digitized by Google

The consensus of opinion was in favor of using the term "oxidized fatty acids" instead of "degras former."

The following method for determination of free fatty acids in moellons was suggested to the committee:

In your opinion, should methods be adopted for the determination of free fatty acids in moellons, and if so, is the following satisfactory? Weigh out 2 grams moellon, dissolve in mixture of 20 cc. alcohol and 20 cc. sulphuric ether, which has been neutralize to phenolphthalein, and titrate with aqueous N/10 NaOH, using phenolphthalein indicator.

TABLE I.—PURE MOELLON, SAMPLE NO. 1.

Moisture.

	Direct heating in platinum dish (Per cent.)	Sand method (Per cent.)	Heating 1 gram in platinum crucible (Per cent.)
Alsop and Cuthbert	32.48	—	32.61
	32.66	—	32.69
Eachus.....	32.90	32.81	—
Esten	32.54	—	—
	32.73	—	—
Faust and Kernahan	32.63	—	—
Orthmann	32.67	—	—
Small and Ames	33.4	34.1	—
Sprague	33.11	—	—
	32.75	32.43	—
	32.54	32.31	—

TABLE II.—PURE MOELLON, SAMPLE NO. 1.

Unsaponifiable.

	Provisional methods for unsaponifiable in sulphonated oil (Per cent.)	Using 5 grams KOH + 50 cc. alcohol, saponifying 3 hours, dissolving soap in 50 cc. water (Per cent.)	Provisional method for sulphonated oil, evaporating alcohol (not refluxing), extracting with sulphuric ether (Per cent.)
Alsop and Cuthbert	0.61	—	—
	0.56	0.41	1.61
Eachus..... ...	0.64	—	—
Esten	0.90	—	—
	0.82	—	—
Faust and Kernahan ...	0.51	—	—
Orthmann	0.39	—	—
Small and Ames.....	0.5	—	—
Sprague	1.03	—	—

Digitized by Google

TABLE III.—ADULTERATED MOELLONS, SAMPLES NO. 2. AND NO. 3.

Unsaponifiable.

	Provisional method for sulphonated oil		Provisional method for sulphonated oil using sulphuric ether		Other methods		
	No. 2	No. 3	No. 2	No. 3.	No. 2	No. 3	Description
Alsop and Cuthbert....	4.03[1]	24.70	8.66[2]	28.34	—	—	10 gr. sample + 5 gr. KOH, 3 hrs. 50 cc. water.
	3.60[1]	24,88	8.83[2]	28.44	3.84	24.17	
Esten.....	5.02[1]	—	—	—	5.83	28.83	5 gr. sample + 2.5 gr. KOH, 1 to 2 hrs., taken up in 50 cc water.
	5.12[1]	—	—	—	—	—	
						27.83	As above, but adding petroleum ether just before saponification was complete.
Faust and Kernahan ..	5.89	28.11	—	—	—	15.93	Sodium methylate instead of KOH.
Orthmann.....	5.11	24.45	9.13	26.69	3.39	18.67	10 gr. sample + 50 cc. sodium methylate, 1 hr. mix with emery, dry, extract 24 hrs. with petroleum ether.
Small and Ames.....	5.5	26.7	—	—	—	—	
Sprague.....	—	—	10.24	30.31	—	—	

[1] Used 50 cc. water in taking up soap.

[2] Persistent emulsion formed; found necessary to extract the dry soap.

Digitized by Google

TABLE IV.—PURE MOELLON, SAMPLE NO. 1.

Oxidized Fatty Acids.

	Eachus method (Per cent.)	Lewkowitsch method (Per cent.)	P. and V. method (Per cent.)
Alsop and Cuthbert	9.11	—	—
	8.95	—	—
Eachus	11.90	—	—
Esten	5.94	—	—
	5.73	—	—
Faust and Kernahan	9.25[2]	—	—
Orthmann	10.49	—	10.93
Small and Ames	—	10.8	—
Sprague	13.01[1]	—	—

[1] Including 0.72 per cent. recovered from acid waters.
[2] Soap broken up in separatory funnel.

Test for mineral acids or alkalis, (by adding methyl orange to the water emulsion of the moellon), and if present, make the necessary correction.

ORTHMANN: Do not think method necessary, but believe the proposed method satisfactory, excepting that if soap is present, there is also a possibility of free fatty acids present, and the suggested correction would be erroneous.

SMALL AND AMES: Latitude should be allowed in quantity of sample taken.

ESTEN: Must be noted that soaps are hydrolized in solutions containing less than 50 per cent. alcohol.

SPRAGUE: Suggest reporting fatty acids as oleic, not using term acid value.

REPORT OF COMMITTEE ON HARD GREASES.

DIRECTIONS: *Paraffine Wax.* Two samples.

No. A Hard Paraffine
No. B Scale Wax } For melting point and free oil.

All other greases. No sample.

Determinations on other greases to be considered are:

Melting point.
Titer test.
Unsaponifiable.
Acid value.

Digitized by Google

No samples will be sent out for this work, as it is believed that given uniform standard methods, chemists using ordinary care will agree very closely. The Committee is requested to draw up methods for these determinations, which are accurate and reliable, and which can be submitted to the Association for adoption.

Paraffine Wax.

Melting Point.—Ordinary methods are not applicable to paraffine wax, and the English and Saybolt methods are commonly accepted as being the most reliable.

The English method reads as follows: "A test tube, about 1 inch in diameter, is filled to the depth of about 2 inches with the melted paraffine, a small thermometer is inserted, and the mass stirred steadily, while the test tube and its contents are allowed to cool slowly. The temperature at which the thermometer remains stationary for about a half a minute is the melting point."

The Saybolt method: This method differs from the English method, in that the melted wax is not stirred; the thermometer being fastened, and the wax being melted in a small cup, which is placed so that the bulb of the thermometer is completely immersed. The wax is allowed to cool slowly, and the temperature at which the thermometer remains stationary for several seconds is regarded as the melting point.

Determine the melting point by these methods, and state which you think is the more accurate.

Free Oil.—Three methods are suggested.

Method No. 1.—The press method, as described by Lewkowitsch, Vol. 3, page 215. Standard presses are made in this country and used by the refiners, but the cost of these presses prohibits the adoption of such a method.

Method No. 2.—Two grams wax are dissolved in 30 cc. ether, cooled to 15° C., and 30 cc. cold alcohol added, the whole stirred thoroughly, filtered, and washed with a mixture of ether and alcohol at 15° C. The filtrate is evaporated to dryness, and taken up with 10 cc. alcohol and ether, cooled to -20° C., and filtered through a jacketed funnel, packed in ice and salt. The filtrate is evaporated, and weighed, and calculated as free oil.

Digitized by Google

Method No. 3.—Formolite reaction. One gram finely powdered wax is digested with 10 cc. acetone for two hours. The mixture is cooled to -15° C., filtered through cotton wool in filter tube surrounded by freezing mixture. The filtrate is evaporated and weighed as free oil.

The Chairman called on Dr. Saybolt of the Standard Oil Co., who stated that in his opinion Method No. 1 was the only dependable method. Nevertheless, all three methods are submitted for your consideration, with the request that you comment fully on their value, and determine the free oil present in the two samples sent you, by whatever method you think advisable.

Can you suggest any other methods for the determination of free oil in paraffine wax?

The table shows the results of the melting point determinations.

Remarks.

Alsop: Prefer English method.

Oberfell: Prefer Saybolt method.

Orthmann: Suggest the Ubbelohde method. If separate method is required for paraffine wax, prefer the English method.

Small: Saybolt method easier of manipulation, and to be preferred, although results slightly lower than the English method.

Sprague: Prefer English method.

Conclusions.

In view of the fact that in only one instance is the difference, by the same operation, between the English and Saybolt methods greater than ½ deg., it seems immaterial which method is adopted. The greatest difference by any two operators by either method is only 1½ deg. The Ubbelohde method does not agree with either method.

Free Oil.

Consensus of opinion indicated that the press method was the most reliable, but that the importance of the determination was

Digitized by Google

out of proportion to the amount of work and trouble necessary to obtain results.

Orthmann made a determination by the following method:

Ten grams of the wax was placed in fine linen, a number of filter papers placed on each side, and put into a letter press for 15 minutes. Sample A showed 0.15 per cent., and Sample B showed 3.17 per cent.

Mr. Saybolt, from whom I obtained the samples, stated that Methods 2 and 3 were not trustworthy. The results in his laboratory by the press method are: Sample A—1.1 per cent. and Sample B—1.5 per cent. He remarks as follows: The sample "A" is a sample that we know positively contains no oil, and it shows 1 per cent. loss in weight, due to particles of wax adhering to the linen mesh as explained to you verbally. So that, even with the best method available (the press), the results show 1 per cent. and more, loss of weight charged to, and which is not oil. This fact has long been recognized by those engaged in this trade, both in this country and abroad, but this method is adhered to because uniformly concordant results are obtained with the machine and the carefully selected linen and paper disks that go therewith.

Small tested Methods 2 and 3 and found 0.06 per cent. free oil in both samples. He offered a method of fractional melting which seems to give more accurate information about a wax than any other method. This method will be published later.

Conclusions.

In view of the conditions brought out by the committee, the chairman does not deem it necessary to propose any method for this determination.

Other Hard Greases.

Melting Point.—Three methods are available.

Method No. 1.—The present provisional method of the A. L. C. A. as described in the A. L. C. A. Official Methods, page 36.

Method No. 2.—The method described by Eachus in the A. L. C. A. Journal, 1912, page 456.

Method No. 3.—The following method has been used by the Chairman with very good results. A thermometer is dipped into the melted grease, so that a film of grease covers the entire bulb.

Digitized by Google

After standing over night, the thermometer is placed in a test tube, lightly corked, so that the bulb is 1 inch from the bottom of the tube. The test tube is suspended over asbestos gauze, the bottom of the test tube being 1 inch above the gauze. A flame is placed beneath, and the temperature gradually raised until the cloud on the bulb disappears.

State which method has given the best results in your experience, and should be submitted for adoption.

Titer Test.—The Chairman suggests the present provisional method, as described in the A. L. C. A. Official Methods, page 35, as being accurate.

Give your opinion as to whether this method should be submitted for adoption.

Unsaponifiable.—Two methods are available.

Method No. 1.—The present provisional method, see A. L. C. A. Official Methods, page 33.

Method No. 2.—The present provisional method for unsaponifiable on sulphonated oil, see page 29 Official Method; this being the same method as suggested for moellon.

State which method in your opinion is the more reliable and should be submitted for adoption.

Acid Value.—The Chairman suggests the present provisional method, see page 31, Official Methods, but suggests the use of N/10 NaOH instead of alcoholic potash, same as was suggested for acid value in moellons.

Give your opinion on this matter, and state whether the above method with its modification, should be submitted for adoption.

Other Hard Greases.

Melting Point.

Alsop: No. 1 should be eliminated. Either No. 2 or No. 3 satisfactory.

Orthmann: Object to all three methods, the Ubbelohde method being the only satisfactory one. A description of this method is as follows:

"The apparatus consists of a thermometer upon the bulb end of which is fastened a metallic tube, perforated with one small hole in the side for the escape of gases. At the lower end, opposite each other, are two arms about ¼ of an inch long; these

Digitized by Google

arms are slit, and form a spring like clamp, into which a small cap is placed. The cap is made of glass with a large opening at one end and a small opening at the other end.

"To use the apparatus, fill the cap with the substance, allow to come to a semi-solid state, then scrape the upper end to level and insert the cap in the metallic tube so that the small opening is downward. By doing this the bulb of the thermometer rests in the center of the substance in the cap. Scrape off the protruding substance from the lower end of the cap and allow to stand at least 24 hours. After which the thermometer is fitted into a large glass tube by means of a cork, which is perforated and slit, the tube is immersed in a beaker filled with water which rests upon an asbestos plate, heat is applied underneath same, and the burner adjusted so that the temperature rises about 1 degree per minute. As soon as the wax commences to melt and protrudes at the lower opening, read the thermometer, then take another reading when the first drop of wax falls from the cap. This is known as the 'drop point.' After using this apparatus 5 years, we have not noticed any irregularity. Melting points were determined by different operators with this apparatus on fats and waxes with concordant results."

SPRAGUE: Do not approve of Method No. 1. Use Method No. 2, but believe Method No. 3 equally good.

OBERFELL: Method No. 1 unsatisfactory. Usually employ Method No. 2, but see no objection to Method No. 3. There is an important class of greases which the Committee does not mention, namely, those greases prepared by blending animal or vegetable greases with paraffine wax. The melting point of these blended greases presents new factors, and the usual methods are not applicable. In view of their rising importance, these greases must be considered.

SMALL: No experience with Method No. 1. As to Method No. 2, prefer to seal capillary tube at lower end, reading the temperature at which the grease changes from opaque to transparent. Have found this method satisfactory, excepting for some greases which are opaque when melted, in which case I use Method No. 3, but take the reading at the temperature at which a drop forms at the bottom of the bulb.

Digitized by Google

Conclusions.

Either Method No. 2 or No. 3 is satisfactory, although Method No. 3 should embody Small's suggestion to take the temperature at which a drop forms on the bulb. It was generally believed necessary to allow the grease to stand 24 hours before making the determination.

Titer Test.—All the collaborators, excepting Sprague, are in favor of the present method.

Unsaponifiables.

Alsop: Method No. 1 should be dropped. Method No. 2 better, but not quite satisfactory; the objections to same being those given for unsaponifiables in moellons.

Orthmann: Method No. 1 satisfactory for most purposes. Where wool grease is present, sodium methylate must be used instead of KOH.

Sprague: Method No. 1 unsatisfactory, but believe Method No. 2 should be adopted.

Oberfell: Favor Method No. 2, as it is the result of the experience of a number of analysts.

Small: Method No. 2 more reliable and preferable, excepting as suggested under moellons, double the amount of KOH should be used.

Conclusions.

Method No. 2 generally satisfactory, and the proposed modification as suggested for unsaponifiables in moellons is no doubt satisfactory.

Acid Value.—Proposed method satisfactory to everyone.

Melting Point of Paraffine Wax.

	English method		Saybolt method		Other methods		
	Sample A	Sample B	Sample A	Sample B	Sample A	Sample B	
Alsop & Cuthbert	127°	119°	127°	118½°	—	—	
Faust & Kernahan	127°	118¾°	126½°	118½°	--	—	
					Ubbelohde method.		
Orthmann	127½°	118½°	127½°	119¼°	121¾°	111¼°	Pro. point
	—	—	—	—	124°	114½°	Drop pt.
Small	126¾°	119½°	126¼°	119¼°	127½°	119°	Small method.
Sprague&Vandriend	126°	118°	127°	119°	—	—	
Standard oil analysis	—	—	126¾°	117¾°	—	—	

Digitized by Google

Discussion.

W. A. Fox asked whether there is a relationship between the melting point of paraffin wax and the amount of oil present.

T. A. Faust replied that he had found no such relation.

F. H. Small described his method of making an approximate separation of the constituents of a paraffin wax, finding their melting points and estimating the proportion of each present. He showed a drawing of the apparatus used. This method will be given at some length with cut of the apparatus in a later issue.

F. P. Veitch called attention to a method of determining directly the proportion of mineral oil in a mixture. Five cc. of the oil to be tested are mixed with 25 cc. of fuming sulphuric acid, exactly 38 times normal. All vegetable or animal oils are destroyed, and about 10 per cent. of the mineral oil. The percentage of mineral oil can then be estimated pretty closely. Mr. Veitch recommended the next oil committee to try this method on mixtures containing wool grease.

T. A. Faust asked for criticism of the method for unsaponifiables suggested by the committee, but none was forthcoming.

NOTES.

Since the death of I. Eitner, announced in the issue of *Gerber* for July 15, no issue of that Journal appeared until Oct. 15, when a double number was published. The office has been transferred to Prague and the editorship assumed by J. Jettmar.

Le Cuir seems to have suspended publication. No issues have been received since the outbreak of the war. *LaHalle aux Cuirs* (Paris), *Gerber-Courier* (Vienna) and *Magyar Boripar* (Buda-Pesth) are coming regularly.

Zeitschrift für angewandte Chemie has not been received beyond the issue for July 31, and only a few issues of *Ledertechnische Rundschau* have come.

The August number of *Collegium*, together with a double number for September and October was received about November 3.

B. Kohnstein (Director of the Vienna Research Station) has been in government service as inspector, and in other ways to look out for the interests of the Royal and Imperial administration in connection with leather purchased for the use of the army.

Digitized by Google

A number of the younger men from the Vienna Institute are in the army, as are several from the Leeds school.

Collegium announces that Dr. Gustav Eberle was killed in battle Sept. 7.

Dr. Edmund Stiasny, head of the Leather Industries Department of Leeds University, was in Austria at the outbreak of the war. Being an Austro-Hungarian reserve officer, he was called into service and has been assigned to hospital duty. Professor Procter has been recalled to take charge of the department.

M. Nierenstein, of Bristol University, has undertaken to serve in the British army as interpreter.

The spirit of fairness and courtesy manifested by M. E. Sadler, vice-chancellor of Leeds University, by Professor Procter and by M. Nierenstein in speaking of scientists who belong to nations now at war with Great Britain is a fine illustration of the strong tendency of scientific research to bring men into a real brotherhood. In contrast to these utterance the language of *some* letters published in our transatlantic exchanges is quite the reverse of broad-minded and reasonable. Certainly the writers of harsh words against men who have committed no fault, but by accident of birth are on the opposite side, will in a few years be ashamed of their present petulance. Many of the greatest soldiers of modern times were men to whom personal animosity and hatred were simply impossible. It is impossible to imagine "Chinese" Gordon or Robert E. Lee reviling a man because he was an "enemy." An early incident in the present war was the death on the field of a young German noble who had been a Rhodes scholar at Oxford. Lying mortally wounded, he was picked up and cared for by Frenchmen, and his words to them were those of a high-minded gentleman. War is terrible, and there are many among the very best men all over the world who believe it to be always unnecessary and therefore always wrong. But it is here, and it becomes the duty of every man who has the instincts of a gentleman, whatever may be his wish in regard to the outcome of the war, to think and speak of all those who are involved in the struggle, whether soldiers or non-combatants, as fellowmen, deserving the courtesy which we should accord to all men. We may rightly hate evil deeds, but to hate a man because he was not born under the same flag as ourselves shows lack of intelligence as well as of some other desirable qualities.

ABSTRACTS.

Meeting of the British Section. *L. T. Rev.*, Nov. 4, 1914. A meeting of the British Section of the I. A. L. T. C. was held at the Leather Industries Department of Leeds University on October 31st. Professor H. R. Procter occupied the chair. The following officers were elected, and it was decided that they should serve until the end of 1916: President,

Digitized by Google

Professor H. R. Procter; Vice-President, Mr. F. O'Brien; Hon. Secretary, Mr. D. J. Law; Hon. Assistant Secretary, Mr. S. Hirst; Treasurer, Mr. M. C. Lamb. It was decided that no member should hold the same office for more than two years. The question of hide powder was next considered, and Mr. H. G. Bennett submitted the report of the hide powder committee. He announced that American hide powder has been passed by the committee, and is therefore the "official" powder for the British Section. A long discussion ensued, and the meeting unanimously adopted the report of the committee.

Improvement in Rapid Tanning. (Patent of G. Durio, of Turin, Italy.) *The Leather Manufacturer,* Nov., 1914. In all the rapid tanning processes heretofore in use, in which concentrated tanning extracts are employed, it has been necessary to keep the skins, while in the tan-liquor, constantly in motion. This mechanical movement requires expensive apparatus which has the drawback of causing more or less damage to the skins while being tanned. The object of the present invention is to get rid of that drawback, while at the same time using concentrated extracts, thereby effecting not only more rapid and sure tanning of the skins, but also an improvement in the quality of the leather produced. The inventor has found that it is not necessary to keep the skins in motion while tanning, even when using concentrated extracts, if the precaution is taken to tan the skins in a perfectly neutral condition. There is also the further advantage that all superfluous tan-liquor can be avoided, thus making a considerable saving.

In carrying out this process, the skins, after unhairing and fleshing in the usual way, and being completely purged of lime and other foreign matters, during which, by the use of acidified water and washing copiously afterwards, and then pressing them, are made absolutely neutral. The skins are opened out and treated with the tan extract. For this purpose, the liquid extracts on the market can be used without thinning out, and the work is preferably done at the ordinary temperature. After opening, the skins are laid in piles and then doubled over in halves, so that the head and tail come together. The liquid tan extract is brushed over the upper surface of the half of the under skin, which is then turned over, and the other half brushed in the same way. The second skin is then treated in the same way, and so on until the pile is completed. They are then left to stand until the tan extract is absorbed, and second coating of extract is given in the same way, repeating until the skins are fully tanned. If this tanning is done in a tank, all superfluous tan-liquor is drawn off. Instead of liquid extracts, dry powdered extract can be used, sprinkling it below the doubled skins. Absorption of the dry tan extract is helped by the moisture of the liquid extract, and the leather will have great denseness and firmness. About a pound of extract at about 25° Bé. is used for each pound of hide. The treatment is repeated three times a day for 8 days, and after that twice a day. A hide of average weight

Digitized by Google

and thickness will require about 20 days to tan fully; heavy skins will take from 25 to 30 days.

New Process of Chrome Tanning. *S. & L. Rep.*, Nov. 5. For the production of one-bath chrome liquors there are two general types of method. The first type of method involves the use of a chromium compound, such as chrome alum, which is rendered basic by the addition of some alkali, such as soda. The modifications in this branch include the use of different alkalis for rendering the salt basic, and also the use of different classes of chromium compounds. The commonest, of course, is chromium alum, of which the active constituent is chromium sulphate. Other chromium salts which have been advanced are chromium formate, chromium acetate, and chromium chloride.

In the second type of method for the production of one-bath chrome liquors, bichromate of potash or soda is taken, and reduced by some reducing material. The chief modification in this class of process rests in the material which is used for the reduction. Both organic and inorganic materials have been used. Of the organic materials probably the most common and the most widely used have been cane sugar, glucose, glycerine and alcohol, whilst the inorganic materials include bisulphite of soda, hyposulphite of soda. According to a recent German Patent taken out by M. F. Hirch, the reduction is carried out by means of a solution of bisulphite of alumina. Bisulphite of alumina is claimed to have the following advantages over hypo or of bisulphite of soda. (1) There is no deposition of free sulphur as with hyposulphite of soda. (2) There is no great evolution of heat as with bisulphite of soda. (3) The deposition of aluminum hydrate is formed in the skin. The reduction should be carried out without the addition of acid. If a solution of bisulphite of alumina of about 14° Bé. be added to a 2 per cent. solution of chromic acid, the complete reduction of the chromic acid is obtained, without any precipitation. If, on the other hand, a solution be used of one-third the above concentration, the reduction of the chromic acid is complete, but at the same time a precipitation is produced in the liquor. The first method of use, that is, with the concentrated solution of bisulphite, is suitable for tannage in one-bath, whilst the liquor produced by the use of the weaker bisulphite solution is only suitable for the tannage in two-baths. The following is given as a practical example:

The skins, washed and soaked as usual, unhaired, fleshed, delimed, pickled and split are submitted to the following treatment: The bath consists of 5 per cent. of bichromate of potash, 2½ per cent. of hydrochloric acid, 180 per cent. of water, calculated on the weight of pelt. The goods are allowed to turn in this liquor for 3½ hours, when they are placed in pile for 12 hours. Finally they are transferred to the second or reducing bath. This bath consists of 36 parts of a solution of bisulphite of alumina of 14° Bé. and 220 parts of water for each 100 parts of pelt. The goods are turned in this liquor for 4 hours, when the tannage

Digitized by Google

should be complete, with the grain even and smooth. According to this patent, the leathers thus tanned are more resistant than those produced by other processes, and can be dyed more easily and more regularly, partly because the deposition of sulphur is avoided and partly because the alumina forms a mordanting which is very favorable to dyeing.

The Investigation of Cellulose Extracts. J. PAESSLER. *Collegium*, 1914 pp. 593-9, August number. The method of the I. A. L. T. C. for vegetable tanning materials is also used for cellulose extracts. The method prescribes that the extract shall be so diluted that 100 cc. of solution shall contain from 0.35 to 0.45 gram tannin. If these limits are passed, the analysis must be repeated. If the extract be an untreated quebracho, with high insolubles, in case the analysis solution is made too strong, the tannin figure will be found too low, while if the analysis solution is made too weak, a high value will be found for the tannin. This result is not due to the hide powder absorbing more material from the weaker solution and less from the stronger. If this were the case, the non-tan figure would be low in the former case and high in the latter. In fact, the non-tan value is found to be the same in both cases, and the difference is due to the transfer of some material from the tannin figure to the insolubles when the solution is too strong. In the case of a material whose content of insolubles is small, such as chestnut extract, the variations caused by changing the strength of the analysis solution are much less. A table is given, showing 7 analyses of the same chestnut extract, using from 8 to 32 grams per liter. The non-tans rise from 11.8 to 12.2 per cent., the tannin falling from 29.7 to 26.6 per cent. Cellulose extracts behave very differently. One was analyzed by the filter method, the amounts taken varying from 9 to 50 grams per liter. The corresponding percentages of "tannin" varied from 27 to 6.8, the "non-tans" varying from 26.9 to 48.2 per cent. Three others were analyzed by both methods. The variations by the filter method are twice as great as by the shake method. By the shake method, varying the quantity from 10 to 50 grams per liter caused a rise in "non-tans" from 28:5 to 37 per cent. In another case, the quantity taken varied from 8 to 21 grams per liter, the "non-tans" rising from 29.3 to 34.6 per cent. Variations of more than 1 per cent. in the tannin content due to differences in the strength of the analysis solution may take place, and yet the amount of "tannin" in 100 cc. be within the prescribed limits. The Freiberg Station uses such quantity as shall bring the amount of "tannin" per 100 cc. as near as possible to 0.4 gram. L. B.

The Use of Cinchonine for the Detection of Sulphite-Cellulose in Tanning Extracts and in Leathers. W. APPELIUS and R. SCHMIDT. *Collegium*, 1914, pp. 597-9. In 1860 Wagner used cinchonine sulphate as a precipitating material for the tannins: (see Dekker, *Die Gerbstoffe*, page 496). He designed this method to be a quantitative one, since he titrated

Digitized by Google

the tan-liquor with cinchonine sulphate solution. The method is, however, not satisfactory, since it was afterward discovered that the precipitation is not complete, and that other materials are thrown down. The authors find that extracts of pure tanning materials, both protocatechin and the pyrogallol group, give with cinchonine sulphate a precipitate in the cold which is entirely soluble on heating. Sulphited extracts leave a cloudiness on heating, but if the solution be acidulated with HCl and heated before adding the cinchonine sulphate, and then filtered, and the cinchonine sulphate added to the clear filtrate, a precipitate is formed in the cold which completely dissolves on heating. If the same proceeding be followed with a sulphite-cellulose extract, a residue is left which on boiling collects in a brown-black mass. The same result is observed when mixtures of the cellulose extracts with tanning extracts are examined, and even when the proportion is quite small the reaction is unmistakable. The water extractive from leather containing sulphite-cellulose extract also shows the reaction. It is not liable to the objection which lies against the Procter-Hirst reaction with aniline hydrochloride, since pure chestnut extract never gives this cinchonine reaction. The authors ask that other chemists test out the method, and give the following directions:

1. Preparation of the cinchonine solution. Into a liter flask put 5 grams cinchonine and 100 cc. water. Add strong sulphuric acid, a drop at a time, until the cinchonine is dissolved. Make up to the mark, shake well, and the solution is ready for use. 2. Carrying out the reaction. To 100 cc. tannin solution of analysis strength (filtration not necessary) add 5 cc. HCl (25 per cent.), boil a short time and cool. Filter off the precipitate which forms during cooling. Sometimes the addition of kaolin is necessary to get an absolutely clear solution. To 50 cc. of the clear filtrate add 20 cc. of the cinchonine sulphate solution. The formation of a precipitate denotes either the presence of a protocatechin tannin or of sulphite-cellulose. Heat to vigorous boiling, but without shaking the flask. If the precipitate dissolves, no sulphite-cellulose was present. The formation of a grayish white mass, darkening on further heating, lumpy and formless is characteristic of sulphite-cellulose material. The pyrogallol tannins, after treatment with HCl give no precipitate, either cold or hot. The attempt of the authors to separate the catechol from the pyrogallol tannins by this means, has not yet been successful. Neradol D gives a precipitate not soluble on heating, but it does not collect in a dark colored mass. The precipitate in this case looks more like a precipitate of silver chloride, distributed about over the bottom of the vessel like sand grains. L. B.

Active Carbonyl and Tannage with Organic Substances. G. POWARNIN (Russia). *Collegium*, 1914, pp. 634-39. The author first specifies objections to Fahrion's oxidation theory of tannage.

It is too simple; the logical consequence is the oxidation of the crude

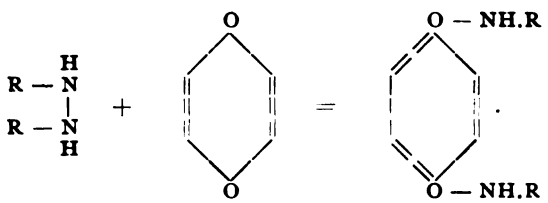
Digitized by Google

hide by the air followed by tannage with a smaller amount of tanstuff. But as well known, the time of storage of the hide does not lessen the amount of tannin required. The hypothesis neglects the chemistry of the tannides and ignores entirely the results of the studies of Emil Fischer and his pupils on the peptides and albuminoids. All the reactions are assumed to be analogous to those of aniline, an aromatic amine, while it has been proved that saturated carbon atoms prevail in the albumins. The theory is not applied to the single chrome bath. In general the oxidation theory can hardly satisfy the practical tanner who is accustomed to fear oxidation of hide in vegetable tannage or the double chrome bath. Since native "quinoids" cannot be identified in all tannides, Fahrion has attempted to prove their formation at expense of the oxygen of the air and water. But it is characteristic of tannides that they precipitate gelatine with absolute exclusion of air. Consequently the proof of quinoid formation by the air is no proof that quinoids are essential to tannage. On this account, Fahrion seems to regard water as the chief agent in quinoid formation.

Neutral solutions of phenols after standing several days in closed vessels were acidified and tested with KI and starch giving considerable color in the case of pyrogallol, pyrocatechin and hydroquinone but none with tannin. The author repeated these experiments with extracts of willow and several species of Rheum and the results were the same as with tannin; all acid solutions on standing, even including phenol, gave negative results. Alkaline solutions standing in the air gave a positive result, but only near the surface exposed to diffusion from the air. Only in alkaline solutions has peroxide formation been proved with certainty and especially with simple phenols, but these have slight tanning power compared with the tannides. The formation of peroxides in neutral solution is so slight that a catalytic action of the hide albumin is assumed in applying Fahrion's theory. He refers to the alkalinity of the collagen, but tannage may be completed in acid solution.

According to Fahrion's theory, the albumins are converted into hydrazines through the Bamberger-Tschirner reaction:

$$2RNH_2 + O = H_2O + R.NH.NH.R.$$

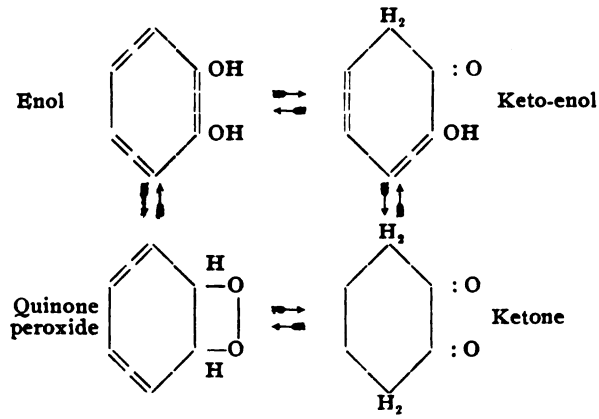


In vegetable tannage Fahrion assumes the formation of *p*-quinones, but most tannides contain *o*-dioxy—or vic. and symm.—trioxy-rings; less than 9 per cent. yield *p*-quinone on oxidation. Nevertheless Fahrion finds an analogy between vegetable and quinone tannage and compares

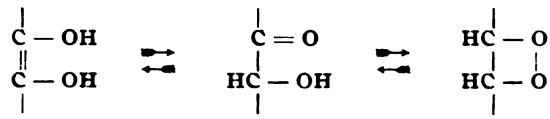
Digitized by Google

tanning with the formation of dianilido quinone. If analogies are to be drawn, it would be more correct to take aliphatic amines since Emil Fischer has shown most albumins are saturated. It seems unlikely that etherial or salt-like compounds such as Fahrion formulates, can exist in leather. They contain linking oxygen atoms and reactions forming such compounds are reversible, whereas in tanning only the first stage (adsorption) is reversible. Another objection to this theory is that it would leave half the tannin in solution in the reduced state and recoverable only after oxidation whereas hide powder withdraws all the tannide in insoluble form. The albumins can be oxidized but not easily which renders the theory of oxidation of collagens by tannides (which reduce silver) untenable.

The author believes a more plausible theory can be advanced, using keto-enol tautomeric formulae (abstr. JOURNAL, 1912, [7] 338) together with the oscillation hypothesis of Baly. Applying these, the tannides may have the following more characteristic forms (typified by pyrocatechin):



α-Diketones are characterized by mobile oxygen. Fahrion himself points out the formation of monoximes of the fatty oxy-acids. The author proposes the following forms for these compounds:

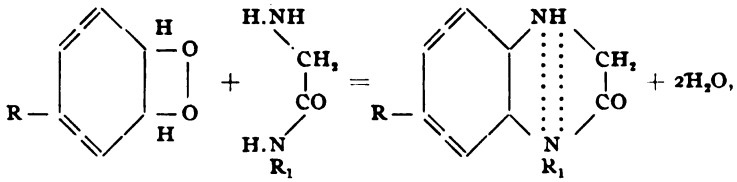


Common to all these tautomeric forms is the carbonyl group with mobile oxygen. This the author calls active carbonyl; it is in evidence whenever equilibrium is disturbed and is the essential factor in tanning. It condenses with various amino-groups splitting off H_2O, or unites with the carbon atom adjacent to the second active carbonyl group. All these reactions, including polymerization, vary in intensity according to ex-

Digitized by Google

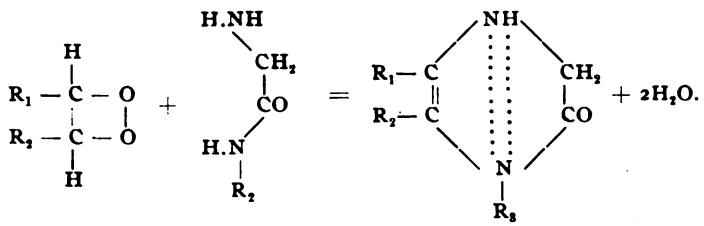
ternal conditions or internal structure. An example of the influence of structure is the lowering of mobility of the oxygen in the series formaldehyde, aldehyde, acetone, with increase in molecular weight. Probably the most stable nitrogen compounds will be obtained when two or more groups of the tan-stuff molecule react forming ring compounds. The *o*- or α- grouping of carbonyl are most favorable for this, and these occur in pyrocatechin, pyrogallol and chamoisage.

The recent studies of Emil Fischer and others on the albumins are referred to. These contain the imido-group—CO—NH—, but the decomposition products are richer in NH_2 groups. Ssadikoff found that after action of NaOH on collagen, the amount of CS_2 adding to amino-groups increased; he calls this "mobilizing the CS_2 receptors." Analogous is Emil Fischer's hydrolysis of a ring compound, diazipiperazin to glycylglycin $H_2N—CH_2—CO—NH—CH_2—COOH$. The tanner also knows well that by action of acids and bases upon hide, its capacity of taking up tannides is increased. This, often called loosening, the author prefers to consider as a chemical change. He gives the nucleus of a formula for leather based on the combination of tannide with diamines;



tannide peptide leather

representing leather as a condensation product of the tetrahydropyrazin ring but not at all as a salt. The quinoid union between the N atoms explains the weak basic character of the compound.



oxy-acid peptide chamois leather

The author recapitulates as follows: The presence of carbonyl is common to all organic tan-stuffs; it results in one way or another from other groups and often appears double in *o*- or *p*-position. The carbonyl at the moment of origin is called active. Active carbonyl as a dynamic conception is found in equilibrium with other groups from which it originates or into which it changes. These groups are the forms enol-peroxide, keto-enol, peroxide-quinone, carbonyl-oxygen linkage, lactone-carboxyl and others.

Digitized by Google

By changing the conditions the rapidity and direction of the processes (polymerization, condensation) can be modified at will when the properties of active carbonyl are more thoroughly and systematically studied.

W. J. K.

Contributions to the Knowledge of Chestnut Extract. LEOPOLD POLLAK. *Collegium,* 1914, pp. 668-72. The author had already shown that chestnut wood varies greatly in character and that very dissimilar liquors and extracts may be obtained from apparently the same sort of wood. Especially the red wood from Corsica yields an extract which gives distinctly the Procter-Hirst reaction. He now reports some additional experimental work on chestnut wood.

The crude fiber was determined by König's method (*Zeit. f. Unters. Nahr. u. Genussm.,* 1898, 1, 1 and 1903, 6, 769). Three grams air-dried wood are boiled (invert condenser) over an oil bath at 133-5 deg. with 200 cc. glycerine, specific gravity 1.23 containing 2 per cent. H_2SO_4 for one hour. The whole is cooled, diluted to 500 cc., again boiled and filtered through a Gooch crucible, washed with hot water, alcohol and ether, and dried at 105 deg. The ash is so slight it may be neglected. To separate lignin the fiber and asbestos are first weighed on a watch glass, the weight of asbestos being found by difference. The mixture is then let stand with 150 cc. pure 3 per cent. hydrogen peroxide and 10 cc. of 24 per cent ammonia in a tall beaker over night. Then 10 cc. of 30 per cent. peroxide are added and after the evolution of oxygen has ceased this is repeated 4 times adding 10 cc. ammonia at the 3d. and 5th. additions. After warming 2 hours upon the water bath, the pure cellulose is collected, washed, dried and weighed in a Gooch; loss = lignin.

The pentoses are determined by distillation, precipitating the furfural with phloroglucin according to Tollens.

Four specimens of wood were examined: (I) from Southeast France. white; (II) Southwest France, yellowish red; (III) South Italy, yellowish red; (IV) Corsica, brown red.

TABLE I.

	I	II	III	IV
Tans	12.50	13.50	13.20	13.20
Non-tans	2.20	1.30	2.20	1.90
Cellulose	27.07	29.95	27.32	27.05
Lignin	10.83	7.10	6.64	6.72
Pentoses	19.06	18.87	18.32	15.28

Probably two forms of lignin exist in the wood, one firmly bound to the cellulose, the other easily split off. The white wood in the above table shows the most lignin, containing less of the separable form, removed by boiling with glycerin. This is important in extract manufacture, since the red color of chestnut liquors as measured by the tintometer depends upon the content of separable lignin. Table I also shows a lower amount of pentoses in wood IV. It is possible that molds or

Digitized by Google

bacteria change a portion of the fixed lignin into the cleavable form and subsist upon the pentoses.

TABLE II.—LEACHED WOOD (RE-COMPUTED AGAINST ORIGINAL TANNIN CONTENT ABOVE).

	I	II	III	IV
Cellulose	29.50	33.12	33.54	31.89
Lignin	9.64	9.47	13.72	12.65
Pentoses	15.55	14.44	13.59	11.49

TABLE III.—COMPOSITION OF CRUDE FIBER.

	Before extraction		After extraction	
	Cellulose	Lignin	Cellulose	Lignin
I.	71.43	28.57	75.37	24.63
II.	80.84	19.16	77.80	22.20
III.	80.45	19.55	70.60	29.40
IV.	80.10	19.90	71.60	28.40

The white, fresh wood differs much from the others. By extraction wood (I) has lost some lignin in the liquor. The increase in lignin in the others may perhaps be attributed to the removal of cellulose by action of the acid. This view is strengthened by the following reasoning: E. Schulze states that the pentosans are found at times in chemical combination with cellulose, consequently less pentoses should have gone into solution from wood I; in fact from 100 total pentoses present originally, 18.42 per cent. have been extracted (Table II) while the others gave up 23.47-25.82 per cent.

The final conclusion is that the firmer the lignin is fixed, the whiter the wood and liquors. The less soluble the pentoses, the better the color of the liquor and perhaps the pentose content may serve as an index. The liquors from woods I and IV contained for 100 parts tans, 4.80 and 19.2 pentoses respectively; the first liquor cleared soon while the second required a long time. In general, the extraction and final treatment must be adapted to each case to secure the best extract. W. J. K.

PATENTS

Process for Softening Leather. U. S. Patent 1,117,912. OTTO RÖHM, Darmstadt, Germany. The skins are treated with a sulphonated oil free from soap and containing a volatile substance soluble in oil.

Machine for Dressing Hides. U. S. Patent 1,117,227. JOHN ORMEROD, Castleton, England.

Ornamented Leather. U. S. Patent 1,115,182-3-4. The leather is stretched in a frame and then treated on the flesh side with a material which causes it to shrink, thereby wrinkling the grain side.

Leather Grading Machine, U. S. Patent 1,113,471. ELMER P. NICHOLAS, Manchester, N. H., assignor to Lacene Manufacturing Co. Cut soles, etc. are passed through the machine. It grades the leather and detects thin spots in the individual pieces.

Digitized by Google

Digitized by Google

Digitized by Google

American leather chemists association Journal
A6
v.9
FORESTRY

TS940 342816
A6
v.9
CALIF. HALL
FORESTRY LIBRARY
amer.

UNIVERSITY OF CALIFORNIA LIBRARY

Digitized by Google

Digitized by Google